**University of Alberta**

*Arsenic Speciation in Natural Water*

by

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A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements for the degree of *Master of Science.*

in

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*To Colin and Olivia.*

**Abstract**

The determination of all arsenic species in water is necessary to provide a complete picture of the biogeochemistry of arsenic and to identify the potential impacts to aquatic ecosystems and to human health. The species of arsenic present, their behaviour and toxicity changes with the biotic and abiotic conditions in the water. In groundwater and freshwater, arsenic is predominantly present as arsenite ($As^{III}$) and arsenate ($As^{V}$). Methylated As species are significant in seawater and estuaries and have been detected in minor amounts in freshwater. The rapid determination of soluble arsenic species ($As^{III}$ and $As^{V}$) in well water was possible using solid phase extraction cartridges. Separation occurred in under five minutes. In groundwater, As may also be present in particulate form in significant amounts. The literature on groundwater As speciation rarely includes this species. Particulate As represented approximately 30 percent of total As in well water samples from Inner Mongolia.

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## LIST OF ABBREVIATIONS

| | |
|---|---|
| $As^{III}$ | Arsenite |
| $As^{V}$ | Arsenate |
| MMA | Monomethylarsenic |
| $MMA^{III}$ | Monomethylarsonous acid |
| $MMA^{V}$ | Monomethylarsonic acid |
| DMA | Dimethylarsenic |
| $DMA^{III}$ | Dimethylarsinous acid |
| $DMA^{V}$ | Dimethylarsinic acid |
| TMA | Trimethylarsenic |
| TMAO | Trimethylarsine oxide |
| $Fe^{II}$ | Ferrous iron |
| $Fe^{III}$ | Ferric iron |
| Mn | Manganese |
| NOM | Natural organic matter |
| SPEC | Solid phase extraction cartridge |
| HGAAS | Hydride generation atomic absorption spectrometry |
| HGAFS | Hydride generation atomic fluorescence spectrometry |
| HPLC | High performance liquid chromatography |
| ICP-MS | Inductively coupled plasma mass spectrometry |

## Chapter 1. Introduction

Arsenic (As) is the twentieth most abundant element in the earth's crust and occurs naturally in the environment in both inorganic and organic forms. As is also released to the environment by anthropogenic activities such as pesticide use, wood preservative, mining and smelting. Human exposure to As by the general population occurs primarily from drinking water and food. In areas of endemic As poisoning such as Bangladesh, India, Inner Mongolia, and Taiwan, the main exposure is through drinking water where inorganic As levels can reach concentrations in the hundreds or thousands of micrograms per liter [1]. The As is released into the groundwater in from natural mineral deposits. Groundwater is the primary drinking water source in these areas.

As and As compounds are classified as Group 1 carcinogens in humans by the International Agency for Research on Cancer [2]. "The agent (mixture) is carcinogenic to humans" and "the exposure circumstance entails exposures that are carcinogenic to humans" [2]. Chronic exposure to high levels of As in drinking water has been linked to skin cancer, bladder cancer and lung cancer, as well as several non-cancerous effects [3-5]. Non-cancerous effects from As exposure include As skin lesions, peripheral vascular disease (blackfoot disease), hypertension, diabetes, ischemic heart disease, anemia and various neurological and respiratory effects [1,3-5]. The reproductive and developmental effects of As exposure have also been reported [4]. The respective scientific committees of the National Research Council and the World Health Organization have reviewed the most significant studies on As exposure, toxicity and metabolism [3-5]. The association of As to internal cancers has led to the increased pressure for stricter guidelines for As in drinking water.

The World Health Organization (WHO) guideline for As in drinking water is 10 μg/L. The Canadian guideline is currently 25 μg/L. The United States recently lowered its maximum

contaminant level (MCL) for drinking water from 50 μg/L to 10 μg/L. To meet these guidelines, methods are needed to first accurately determine the amount of As and the amount of each species in each well. The speciation is important because some species of As are more toxic than others and some species are more easily removed from aqueous environments. As is present in a variety of inorganic and organic chemical forms in water. This is a result of chemical and biological transformations in the aquatic environment. The specific As compound present determines its toxicity, biogeochemical behaviour and environmental fate. In natural waters, As is typically found in the +5 and +3 oxidation states [6-11]. The most common As compounds detected in water are arsenite ($As^{III}$) and arsenate ($As^{V}$). Monomethylarsonic acid ($MMA^{V}$), monomethylarsonous acid ($MMA^{III}$), dimethylarsinic acid ($DMA^{V}$), dimethylarsinous acid ($DMA^{III}$), and trimethylarsine oxide (TMAO) have also been detected in water. Several reviews provide important additional information regarding the cycling and speciation of As in water and the environment [3,5,6,8,9,12,13].

The first objective of this thesis is to review the literature on As speciation in natural water, including groundwater, fresh surface water, seawater and estuaries (Chapter 2). The second objective is to describe a method that provides rapid determination of soluble $As^{III}$ and $As^{V}$ in water (Chapter 3). In Chapter 4, the concentration of particulate As is determined in Inner Mongolia well water samples and the potential implications of this As species are discussed.

**References**


[1] D. Chakraborti, M.M. Rahman, K. Paul, U.K. Chowdhury, M.K. Sengupta, D. Lodh, C.R. Chanda, K.C. Saha, S.C. Mukherjee, Talanta 58 (2002) 3.

[2] IARC, in, Volume 23 Supplement 7 http://193.51.164.11/htdocs/Monographs/Suppl7/Arsenic.html., 1987.

[3] NRC, Arsenic in Drinking Water, National Academy Press, Washington, DC, 1999.

[4] NRC, Arsenic in Drinking Water: 2001 Update, National Academy Press, Washington, DC, 2001.

[5] WHO, Environmental Health Criteria 224: Arsenic and Arsenic Compounds, World Health Organization, Geneva, 2001.

[6] J.F. Ferguson, J. Gavis, Wat. Res. 6 (1972) 1259.

[7] A.H. Welch, M.S. Lico, J.L. Hughes, Ground Water 26 (1988) 333.

[8] S. Tamaki, W.T. Frankenberger, Rev. Environ. Contam. Toxicol. 124 (1992) 79.

[9] W.R. Cullen, K.J. Reimer, Chem. Rev. 89 (1989) 713.

[10] J.A. Cherry, A.U. Shaikh, D.E. Tallman, R.V. Nicholson, J Hydrol. 43 (1979) 373.

[11] M.O. Andreae, Limnol. Oceanogr. 24 (1979) 440.

[12] N.E. Korte, Q. Fernando, Crit. Rev. Environ. Cont. 21 (1991) 1.

[13] A.H. Welch, Ground water 38 (2000) 589.

## Chapter 2. Literature Review of Arsenic Speciation in Natural Water*

### 2.0 Introduction

A knowledge of the speciation of As in natural water is important because the bioavailability and the physiological and toxicological effects of As depend on its chemical forms. Arsenic occurs in a variety of chemical forms in water, and this is a result of many chemical and biological transformations in the aquatic environment [1]. The mechanism of transport of As depends on the chemical species present.

The main As compounds detected in natural waters are arsenite [$As^{III}$], arsenate [$As^{V}$], monomethylarsonic acid [$MMA^{V}$], monomethylarsonous acid [$MMA^{III}$], dimethylarsinic acid [$DMA^{V}$], dimethylarsinous acid [$DMA^{III}$], and trimethylarsine oxide [TMAO] (Tables 2-1 and 2-2). Since there are large differences in chemical behaviour and toxicity among the As species, the determination of speciation is very important in the study of the biogeochemistry of As. In oxygen-rich waters with high redox potentials the $As^{V}$ species that are stable in water are $H_3AsO_4$, $H_2AsO_4^-$, $HAsO_4^{2-}$ and $AsO_4^{3-}$ [2,3]. $As^{III}$ species, which typically exist in oxygen-deficient waters may include $H_3AsO_3$, $H_2AsO_3^-$ and $HAsO_3^{2-}$ [2,3]. However, in most natural waters, $As^{III}$ is present as $H_3AsO_3$ (its pKa values are 9.23, 12.13 and 13.4) [2,4-6]. The pKa values of $As^{V}$ are 2.22, 6.98 and 11.53 [5]. At natural pH's, $As^{V}$ is usually present as $H_2AsO_4^-$ and $HAsO_4^{2-}$ [2,3,6].

Arsenic speciation and distribution is affected by redox processes. These processes are complicated by physicochemical processes such as adsorption, coprecipitation, desorption and biological phenomena such as uptake and regeneration. Factors such as pH, Eh (thermodynamic redox potential), solution composition, competing and complexing ions, mineralogy, reaction kinetics, and hydraulics of water systems can all potentially affect the As speciation and

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concentrations. This chapter will examine the observed speciation of As detected in groundwater, surface freshwater, estuarine/coastal, and seawater and some of the variables that affect the speciation. Several reviews have discussed work on these topics [3,5,7-9]. The highest concentrations of As are found in groundwater which is a drinking water source for many countries. The focus of this review is on As speciation and behaviour in groundwater.

## 2.1 Groundwater

The major As species in groundwater are the inorganic arsenite ($As^{III}$) and arsenate ($As^{V}$). Extremely high levels of inorganic As in well water have been attributed to devastating As endemic episodes [10-14]. In West Bengal, India, 47 of 47000 tubewell samples contained total As concentrations above 1000 μg/L [12] . One hundred and eighty-nine of 9640 tubewell water samples from Bangladesh contained more than 1000 μg/L [12]. In Inner Mongolia, China, approximately 20% of 305 shallow wells tested measured As concentrations between 50 μg/L and 1860 μg/L and 55% of deep wells had concentrations between 50 μg/L and 360 μg/L [13]. In the groundwater of La Pampa, Argentina, the As concentrations showed high spatial variability over short distances [15]. The dissolved As spanned over 4 orders of magnitude (<4-5300 μg/L).

Arsenite ($As^{III}$) , $As^{V}$, $MMA^{V}$, $DMA^{V}$ and trimethylarsenic (TMA including trimethylarsine and trimethylarsine oxide) have been detected in ground water (Tables 2-1 and 2-2). The concentrations of organic As species are typically low in groundwater. It is important to note that the majority of studies included in this review report the concentrations of As in problem areas. The concentrations of As in groundwater in endemic areas are not representative of all groundwater.

Arsenic is present in groundwater primarily as a result of the dissolution of naturally occurring As-rich minerals and organic matter [9,16-19]. There are two main conditions that can cause a significant release of As. The first is high pH conditions which can lead to the desorption

of adsorbed As from mineral oxides or can prevent the adsorption of As. The desorption of As may be promoted by a high pH or the introduction of a competing adsorbent [8,9]. The lower adsorption at higher pH may be due to the formation of a negative surface charge on ferric oxyhydroxide. This may result in an electrostatic repulsion between the sorbent and the As anion. The typical pH range of groundwater is pH 6.5-8.5 [8,9]. The second condition is the development of strongly reducing conditions at near-neutral pH values, leading to the desorption of As from mineral oxides and to the reductive dissolution of Fe and Mn oxides.

Groundwater aquifers are normally in a reduction state [20-22]. The reductive dissolution of As-rich Fe oxyhydroxides results in the release of As [8,21-24]. This process is considered to be a more likely As source than is pyrite oxidation [21]. The process dissolves Fe oxyhydroxide and releases to groundwater both $Fe^{2+}$ and As. The reduction of As-rich Fe oxyhydroxides may be influenced by microbial action [8,21,25]. The microbial mediated reduction of $As^{V}$ sorbed to ferrihydrite in the absence of significant reductive dissolution of the $Fe^{III}$-solid phase has been studied [26]. A *Clostridium sp.* strain was able to reduce aqueous $As^{V}$ within one day, however, the microbe was not able to cause a significant desorption of $As^{V}$ from ferrihydrite in 24 days. The sorbed As remained predominantly as $As^{V}$ and was not solubilized during microbial growth. Chemolithotrophic bacteria have been attributed to the reduction of As-rich hematite and maghemite in the current tailings impoundment at Campbell Mine in Balmertown, ON, Canada [27].

Arsenic may be leached into groundwater because of an interaction between carbonate ions ($HCO_3^-$) and As minerals in rocks [17,28]. The reductive dissolution of Fe oxyhydroxide generates $HCO_3^-$ according to the following reaction[21]:

$$4FeOOH + CH_2O + 7H_2CO_3 \rightarrow 4Fe^{2+} + 8HCO_3^- + 6H_2O$$

Large concentrations of phosphate, bicarbonate, silicate and possibly organic matter may enhance the desorption of As because of competition for adsorption sites [9]. When studying the effect of zerovalent Fe in removing inorganic As species from water, silicate, chromate, and molybdate caused strong inhibition of As removal, followed by carbonate and nitrate, whereas borate and sulfate only caused slight inhibition to $As^{III}$ removal [29]. Model calculations confirmed that the sorption of carbonate at common groundwater concentrations reduces the sorption capacity of As on ferrihydrite significantly [30]. Sediments containing high amounts of sorbed As are deposited in surface water with low carbonate concentrations and subsequently the sediments become exposed to groundwater with a high dissolved carbonate content, and As is mobilized by displacement from the sediment surface [30].

Sulfide and pyrite minerals can be a source or sink for As and in oxygen rich water, the dissolution of sulfide minerals may contribute As to ground and surface water [8]. The precipitation of sulfide minerals, which can occur in sulfide-rich water, can in turn remove As from water [1,8]. Arsenopyrite (FeAsS) is the most common As mineral. The oxidation of arsenopyrite is an exothermic process and releases sulfates and As to the groundwater by the following reaction [8,18,19,28]:

$$FeAsS + 3.25O_2 + 1.5H_2O = Fe^{2+} + SO_4^{2-} + HAsO_4^{2-} + 2H^+$$
$$\Delta H = -324 \text{ kcal/mol}$$

This oxidation process can be expediated by bacteria [8]. Arsenopyrite is stable at high pH and low redox potential and becomes less stable as slightly more oxidizing waters move through resulting in dissolution [19]. Secondary mineral phases may be formed from this oxidation process [18]. In the Zimapan Valley, Mexico, the main identified As minerals were arsenopyrite (FeAsS) and the secondary mineral scorodite ($FeAsO_4.H_2O$) [19]. Arsenopyrite oxidation can lead to precipitation of scorodite under acidic conditions (pH < 1.5), but this product commonly

breaks down to Fe oxide [8,28]. Scorodite is stable at low pH and high Eh [19]. In aqueous settings, scorodite gradually alters to limonite releasing As through the following reaction [19]:

$$FeAsO_4 \cdot 2H_2O \rightarrow Fe(OH)_3 + H_2AsO_4^-$$

### 2.1.0 Species Stability, Preservation and On-site Speciation

$As^V$ has commonly been reported as the predominant water-soluble species in groundwater. However, studies now show that $As^{III}$ may be present in higher concentrations than $As^V$ in some groundwater . $As^{III}$ was determined to be the predominant species in most groundwater samples measured from tanks and wells in Hanford, Michigan [31]. In eleven of fourteen wells and three of four tanks, $As^{III}$ was present as 86 + 6% of the total As [31]. In the Blackfoot Disease Area (BFD) in Taiwan, $As^{III}$ was the predominant species with an average $As^{III}/As^V$ ratio of 2.6 [32]. In samples from Bangladesh, $As^{III}$ was present as 30-98% of total As [22]. Approximately 60% of the samples contained 10 μg/L or more $As^{III}$ , 44% of the samples contained 50 μg/L or more $As^{III}$ and about 6% of the samples contained 500 μg/L $As^{III}$ [22]. In groundwater and acid mine drainage samples, the $As^{III}$ concentration ranged from 0-90% [33]. The kinetic oxidation of $As^{III}$ to $As^V$ is slow compared to many other oxidation processes and $As^{III}$ can therefore concentrate and travel great distances from As source areas [34].

The procedures used for sample handling and analysis and the sample matrix itself may result in the oxidation of $As^{III}$ to $As^V$ [35-38]. Studies of the effectiveness of various methods of preservation and storage of water samples are at best contradictory. A preservation method which applies to all As species has yet to be developed.

Edwards et al. [39]used ascorbic acid and HCl as preservatives in different types of water. In spiked synthetic water both preservatives were able to maintain the concentration (4 μg/L) of $As^{III}$ and $As^V$ for 28 days. In spiked natural waters with ascorbic acid, $As^{III}$ slowly

transformed to $As^{V}$ during 8 days of observation. In three well waters, EDTA was able to preserve the original $As^{III}$ + $As^{V}$ concentration for 10 days. After 14-27 days, approximately 2-3 µg/L of $As^{III}$ was converted to $As^{V}$. Both $HNO_3$ and HCl caused $As^{III}$ oxidation to $As^{V}$ in spiked deionized water and Ottawa River samples [40] and groundwater and acid mine drainage samples [33]. Bednar et al. [33] used $HNO_3$ and found that the species distribution was maintained as long as the samples were not exposed to ambient light which would result in the photo-oxidation of $As^{III}$ to $As^{V}$. Some studies recommend freezing aqueous samples at –20°C as the best way to preserve the species [41]. Lindemann et al. [42] tested the storage of water samples at temperatures of –20°C , 3°C and 20°C and found that 3°C to be the most effective temperature to preserve As species.

Difficulties arise when trying to preserve As species in iron ($Fe^{III}$) rich waters. In $Fe^{III}$ rich drinking waters, soluble As species can form insoluble $Fe^{III}$ precipitates. The formation of these precipitates results in a loss of aqueous As, which results in an underestimation of the As species present. In $Fe^{III}$ rich water samples, Daus et al. [43] used 0.01 M phosphoric acid ($H_3PO_4$) and storage at 6°C and As species remained relatively unchanged for 5 days. To prevent $Fe^{III}$ precipitation, HCl [44] and EDTA [33,45] have been used to preserve As species in Fe-rich drinking waters. The preservation of $As^{III}$ in $Fe^{III}$ containing waters was not possible with only the addition of HCl [44]. Borho and Wilderer [44] added HCl (pH <2) and excess $Fe^{II}$ to groundwater samples, and $As^{III}$ was stable in solution for 1 week. The low pH should prevent microbial transformations. The distribution of $As^{V}$ and $As^{III}$ remained stable for approximately 120 hours when EDTA was added to groundwater and acid mine drainage samples [33]. Reagent water that was fortified with $As^{III}$, $Fe^{III}$ and EDTA showed less than a 1µg/L change in the $As^{III}$ concentration in 16 days [45].

Methylarsenicals are more stable than inorganic As in water [46,47]. Jokai et al. [47] found that solutions of organic As species were stable during long-time storage, however, solutions of inorganic species at 0.5 μg/mL or 1 μg/mL stored at 4°C were stable for 21 days and showed some transformation after 29 days of storage. At 25°C it appeared that solutions with the highest concentrations of As species (20 μg/mL or higher) could be stored without a significant loss of species [47]. However, at lower concentrations, inorganic species transformation was observed by the end of the first week [47].

Methods of on-site separation of $As^{III}$ and $As^{V}$ species immediately after water sample collection are particularly useful. The portability of the methods allows for complete separation and no preservation of the samples is needed. Ficklin [48] used strong anion exchange resins to separate soluble $As^{III}$ and $As^{V}$ in groundwater. Le et al. [35] used disposable solid-phase cartridges for the speciation of particulate and soluble As. A measured volume of a water sample is passed through a 0.45 μm membrane filter and a silica-based strong anion exchange cartridge connected in serial. Particulate As is captured on the filter and the anion exchange cartridge retains $As^{V}$. $As^{III}$ ($H_3AsO_3$) is not retained and is detected in the effluent. The anion-exchange cartridge is subsequently eluted with 1M hydrochloric acid (HCl) and the eluent is analyzed for $As^{V}$ concentration. Kim also used a portable ion-exchange method with a strong anion-exchange resin in the field and found that neither $As^{V}$ nor $As^{III}$ changed its oxidation state during the experiment [36]. However, upon examination of samples from private wells in Genesee County, Michigan, the oxidation of inorganic $As^{III}$ to $As^{V}$ occurred within three days of storage in a refrigerator [36]. Immediately after sampling, $As^{III}$ represented 82-95% of the total As and after three days, 25-30% of the original $As^{III}$ was oxidized to $As^{V}$ [36]. In another study, $As^{III}$ dropped to approximately 70% of its original value after 6 months of storage [37].

Miller et al. [49] used an onsite ion exchange method to separate As species in aqueous solution and found that organic As species eluted with $As^{III}$, and therefore, caution should be exercised in the analysis of As species to determine the toxicity of As in drinking water. Organic species and particulate As could be detected as $As^{III}$ using this method. A microfabricated gold ultramicroelectrode array has also been used for the onsite analysis of As in groundwater [50]. In countries such as Bangladesh with a serious As problem affecting up to 70 million people and 6-11 million wells to be tested, the priority is the rapid detection ability and ease of use of the method and not necessarily the sensitivity. Field test kits are used to provide rapid detection [28,51]. These methods are commonly based on the reaction of arsine gas with mercuric bromide and can achieve a detection limit of about 10 μg/L by visual comparison of the coloured stain against a colour calibration chart [51].

### 2.1.1 Predicted and Observed Soluble Arsenic Speciation

The thermodynamic redox potential (Eh) and pH are the most important factors controlling As speciation (Figure 2-1). Thermodynamic considerations alone predict that $As^{V}$ should be the predominant As species stable in oxygenated waters and $As^{III}$ should be the only As species stable in reductive environments [2,3]. However, the chemical species of As in aqueous systems usually are not at equilibrium status because of slow rates of redox reactions [28]. $As^{III}$ and $As^{V}$ have been detected in both oxidizing and reducing environments. Microbial mediated reductions and oxidations of As play an important role in the transformation of As in all environmental mediums [28]. In the natural environment, the rates of both $As^{III}$ oxidation and $As^{V}$ reduction reactions are controlled by micro-organisms and can be orders of magnitude greater than under abiotic conditions [3].

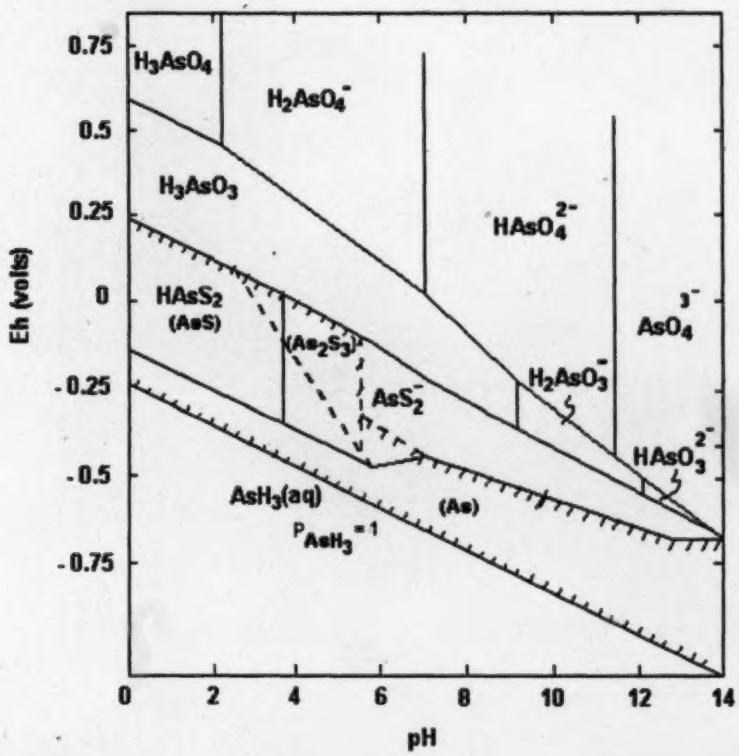


Figure 2-1: Eh-pH diagram for As at 25°C, 1 atm with total As $10^{-5}$ M and total sulfur $10^{-3}$ M, solid species are enclosed in parentheses in cross hatched area, which indicates solubility less than $10^{-5.3}$ M[2].

$As^{V}$ is favored thermodynamically in water with a positive redox potential and high ionic strength [3,28,52,53]. However, $As^{III}$ has also been detected as the predominant species in groundwater under oxidative conditions [23,52]. At redox potentials typical of natural waters, Eh-pH diagrams suggest that decreases in pH should increase the amount of $As^{III}$ present compared to $As^{V}$ [2,3,28] (Figure 2-1). However, this is rarely the case. In well waters, Del Razo et al. [54] could not find a relationship between the $As^{III}/As^{V}$ ratio and the pH (6.3-8.8) of the samples. In this study, the extraction process from the aquifer could have resulted in changes in the oxidation state [54]. The dissolved total As should correlate positively with pH and alkalinity [15]. However, in groundwater in the United States, the correlation between pH and the amount of dissolved As present was very slight [55].

Dissolved organic carbon concentrations were found to be considerably higher in wells during times when $As^{III}$ was present in contaminated wells in Kulheim, Germany [52]. In one well with a positive redox potential, $As^{III}$ was the dominant species. The authors suggest that this was due to the stabilization of $As^{III}$ by organic matter [52]. The oxidation of arsenite by oxygen occurs very slowly [56]. In a study where pure oxygen and air were used for oxidation, only 57% and 54% of $As^{III}$ respectively, were oxidized after five days [56]. Planar-Friedrich et al. [57] examined 19 wells in the Rioverde basin, Mexico and six of them showed higher concentrations of $As^{III}$ than $As^{V}$. The authors hypothesize that the lacustrine sediments probably contain organic rich strata and consequent biological degradation leads to oxygen consumption.

### 2.1.2 Particulate Matter

Studies often overlook the amount of particulate As present in drinking water. The water samples are usually filtered before analysis which can remove a considerable amount of As adsorbed to particulate matter. Suspended matter in natural water may occur as undissolved

mineral and organic species that bind heavy metals. Arsenic adsorbs to particulate and this fraction can be substantial [18,35,55]. Particulate As is described in more detail in Chapter 4.

## 2.2 Fresh Surface Water

The geochemical cycle of As in fresh surface water and the environmental biochemistry and speciation of As have been examined in detail [3,7,58]. The concentration of As in freshwater systems varies considerably with the geological composition (bedrock lithology) of the drainage area and the extent of anthropogenic input (Tables 2-1 and 2-2) [9]. Geothermal inputs are the source of elevated As concentrations in some lakes and rivers [59-61]. Chemical weathering and anthropogenic activities may also result in the contamination of surface water.

Typical concentrations of As in freshwater have been reported as 0.1 – 80 $\mu g/L$ [3,9,62]. The major As species in freshwater are inorganic $As^{III}$ and $As^{V}$ (Table 2-1). Minor amounts of $MMA^{V}$, $DMA^{V}$ and methylated $As^{III}$ species can also be present in natural waters [3,63-66] (Table 2-2). In rivers, As is predominantly bound to sediments.

### 2.2.0 Fresh Surface Water Arsenic Speciation

In lakes, the speciation of As will change throughout the water column due to different conditions in the epilimnion (upper oxic layer), the thermocline (zone of rapidly changing temperature), and hypolimnion (bottom oxygen deficient layer). In Lake Pavin, France, $As^{V}$ represented 88-95% of total dissolved As in the oxic compartment and $As^{III}$ was the dominant species in the anoxic zone (50-90%) [67]. However, $As^{III}$ has been detected throughout the water column of a lake and $As^{V}$ has been detected in the lower anoxic layers of lakes [66,67]. Sohrin et al. [66] found that the $As^{III}/As^{V}$ ratio was lower during more extensive anoxia suggesting that the rates of reduction and oxidation may vary depending on physicochemical conditions and biotic composition. $As^{V}$ was the dominant species present in the hypolimnion of Lake Biwa through all

seasons [66]. During summer stratification in Lake Griefen, Switzerland, $As^{V}$ was replaced by $As^{III}$, but in the anoxic hypolimnion, $As^{V}$ remained the dominant species [68].

A slow reduction rate from $As^{V}$ to $As^{III}$ may be responsible for the incomplete response of the As redox couple to reducing conditions in the hypolimnion [2,67,69]. The observed disequilibrium speciation in the anoxic layers of Lake Pavin, France is attributed to a kinetic control of the $As^{V}$ reduction reaction [67]. The calculated theoretical $As^{III}/As^{V}$ ratio was calculated to be 1010 in the redoxcline (50-65m), however, the observed ratio was measured at 1.05 [67]. In Upper Mystic Lake in the Aberjona Watershed, USA, As speciation also appeared kinetically controlled [70]. $As^{III}$ represented 30% of the total As for the colder months and 48$\pm$7% in the summer and fall. $As^{V}$ decreased from 62$\pm$28% of the total As in the winter and early spring to 28$\pm$13% in the summer months.

The presence of $As^{III}$ and methylarsenic in the surface water of Upper Mystic Lake suggests biological transformation [70]. Laboratory studies have shown that the oxidation of geothermal $As^{III}$ in stream waters of the Eastern Sierra Nevada are likely microbially mediated [71]. Dissimilatory reduction of $As^{V}$ may also occur under aerobic conditions when facilitated by microorganisms [72]. Microbial populations from *Sphingomonas*, *Caulobacter*, *Rhizobium*, and *Pseudomonas* genera were isolated from limed reprocessed mine tailings, and all were capable of rapidly reducing $As^{V}$ in aerated serum bottles [72].

### 2.2.1 Mobility of Arsenic

The distribution and mobilization of the As species in freshwater sediments is controlled by redox potentials, pH, microbially mediated transformation and adsorption processes [6,28,73]. The mobility of As may increase as the sediment environment becomes more reducing. Reducing conditions beneath the sediment water interface results in the dissolution of Fe oxyhydroxides and the release of $As^{V}$ to the porewater and overlying water. The $As^{V}$ is either reduced to the

more mobile $As^{III}$, or reductive dissolution of Fe occurs [65]. Reductive dissolution of ferric hydroxides is a microbially mediated process and two strains of dissimilatory $Fe^{III}$-reducing bacteria were isolated from surface sediments of Lake Coeur D'Alene, Idaho contaminated with mine tailings [74]. Dissolved $Fe^{II}$ concentrations greater than 41 $\mu g/L$ in Lake Coeur D'Alene at a depth of 10 to 15 cm indicates that oxygen is absent and Fe is being reduced in this region[75]. In laboratory studies, an arsenate-reducing microorganism native to the Aberjona Watershed was able to dissolve 38% of the As present [73].

In rivers, As is mainly bound to sediments [6]. Organic rich sediments create conditions that reduce $As^{V}$ to $As^{III}$ and cause possible desorption of the less strongly held $As^{III}$. In one study it was shown that both $As^{V}$ and $As^{III}$ have strong affinities for ferrihydrite and $As^{III}$ can be retained in much larger amounts than $As^{V}$ at high pH (>7.5) or at high As concentrations in solution [76]. In fact, this relationship between As and $Fe^{III}$ oxyhydroxides can be used to stabilize available As in highly contaminated mine tailings. Kim et al. [77] found that in mixtures of $As^{III}$ and $Fe^{III}$ solutions there was increased As sequestration via interaction with amorphous Fe compounds.

$As^{V}$ is not necessarily reduced to $As^{III}$ under reductive conditions. In laboratory experiments, the bacterium *Shewanella alga* strain *BrY* promoted As mobilization from a crystalline ferric arsenate as well as from sorption sites within whole sediments [74]. $As^{V}$ sorbed to sediments from Lake Coeur d'Alene, a mining impacted environment enriched in both Fe and As, was solubilized by the activity of the bacterium *Shewanella alga BrY* and $As^{III}$ wasn't detected [74]. Therefore, As mobility can be enhanced by the activity of dissimilatory Fe-reducing bacteria in the absence of As reduction.

Redman et al. [78] found that when natural organic matter (NOM) and As were incubated together with hematite, the NOM dramatically delayed the attainment of sorption equilibrium and

diminished the extent of sorption of both $As^{III}$ and $As^{V}$. Competition between NOM and As for sorption thus may be an important process in natural waters, suggesting that NOM may play a greater role in As mobility than previously recognized [78].

### 2.2.2 Seasonal Variation

Arsenic concentrations and species vary seasonally [66,70,79,80]. In the summer, hypolimnion waters spiked with $DMA^{V}$ decreased less than 20% whereas in the winter in oxic deep waters the decrease was 100% [58]. The dominant redox reactions of inorganic As in Lake Greifen, Switzerland in the epilimnion were biologically mediated reduction by phytoplankton in summer and oxidation of $As^{III}$ by manganese (Mn) oxides in fall [68]. In Lake Biwa, Japan, $As^{V}$ was the dominant species during the winter mixing and decreased during summer stagnation [66]. $As^{III}$ increased in spring and fall and $DMA^{V}$ was the dominant species in summer [66]. $MMA^{III}$ and $DMA^{III}$ were present in small amounts in the epilimnion and hypolimnion of Lake Biwa and did not show significant seasonal change [66]. $DMA^{III}$ is thermodynamically unstable in oxic aquatic solutions [81]. The concentrations of methylarsenicals may also vary year by year. Hasewaga et al. [65] reported that $MMA^{III}$ was uniformly distributed throughout the water column of Lake Biwa in 1993 but increased throughout the water column in April and October 1994.

### 2.2.3 Effects of Sulfide on Arsenic Speciation

The presence of sulfide will complicate As speciation. Sulfide will affect the species of Fe, Mn, and As present and their solubilities [2,3,67] (Figure 2-1). In the presence of extremely high concentrations of reduced sulfur, dissolved As-sulphide species can be significant [9]. The degradation of organic matter is responsible for elevated hydrogen sulfide concentrations and low redox potential in natural waters [67]. In the presence of sulfide and under low oxygen conditions, Fe sulfide minerals may form and As may coprecipitate with Fe sulfides as

arsenopyrite (FeAsS) or form As sulfides [2,3]. At pH values below approximately 5.5 and Eh values at approximately 0V, realgar (AsS) and orpiment ($As_2S_3$) will form [2]. In the spring, there was 22% sorbed $As^{III}$ and 78% As sulfide species residing in the solid phase in the anoxic layers of a wetland [82]. Arsenic sulfides may occur as a result of microbial reduction of sulfate and arsenate [82]. In a study using municipal sewage sludge, Carbonell-Barrachina et al. [83] found that at a redox potential of –250mV, As solubility was controlled by the formation of insoluble sulfides and as a result soluble As contents dramatically decreased as compared to levels measured at 0 mV. The increases of both $As^{V}$ and $As^{III}$ in the water column of Upper Mystic Lake were also closely correlated with that of sulfide [84]. Dissolved $As^{III}$ is thermodynamically favored in sulfate-reducing waters and is not as strongly adsorbed as $As^{V}$ [67]. As the release of sulfide diminishes, $As^{III}$ is oxidized to $As^{V}$ and $As^{V}$ is scavenged by particles [84].

### 2.2.4 Effects of Phytoplankton

The uptake of $As^{V}$ by phytoplankton can lead to As transformation in aerobic aquatic environments. It is not clear whether $As^{III}$ and methylarsenicals are produced directly by phytoplankton or indirectly by degradation due to the complex interplay of biotic community differences and excretion or degradation pathways. The freshwater algae *Closterium aciculare* was able to produce $As^{III}$ and methylarsenicals in the presence of $As^{V}$ in culture mediums [81]. $As^{III}$ and $DMA^{V}$ were the major species present in the culture medium and the minor species included $MMA^{V}$, $DMA^{III}$, and $MMA^{III}$ [81]. In the epilimnion, the $As^{III}$ is likely produced by phytoplankton, whereas in the hypolimnion it may have been released by sediments or formed by the reduction of $As^{V}$ in the water column [66].

With the exception of two alkaline lakes (Mono and Pyramid), the methylated forms of As comprised an average of 24% of the total dissolved As in the surface waters of lakes examined

by Anderson & Bruland [58]. The average total methylarsenic concentration was 0.7% of total dissolved As in lakes contaminated by gold mines [85]. $MMA^{III}$ and $DMA^{III}$ (intermediates in the biosynthesis of organoarsenicals) have been found in the aerobic surface waters of Lake Biwa [65]. Recently, $MMA^{III}$ has been detected in various strains of freshwater phytoplankton [81]. In Lake Biwa, the dominant species present was $DMA^{V}$ and was produced in the photic zone and also in the hypolimnion [65]. $DMA^{V}$ and $As^{III}$ have been observed in the oxic euphotic zone in the northern basin of Lake Biwa and in anoxic conditions [66]. $DMA^{V}$ was also detected in and below the photic zone of Lake Biwa [65].

Chlorophyll *a* is often used as a surrogate measure of the amount of phytoplankton in a water sample. The relationship between Chlorophyll *a* and methylarsenical concentration is sometimes used to determine if $As^{III}$ and organoarsenicals are being directly produced by phytoplankton. However, not all studies have found a significant correlation between these variables [58,66]. When single sample days were examined, there was some linear correlation suggesting that $DMA^{V}$ and $As^{III}$ in Lake Biwa do originate from phytoplankton and are dependent on sampling time (the species and amounts of phytoplankton present may vary throughout the year) [66]. Abdel-Moati [86] found a correlation between the methylation of As and freshwater diatoms using Chlorophyll *a* as the measurement ($r^2$ =0.8827). Hasewaga [65] also found an association between Chlorophyll *a* and $As^{III}$. In Lake Biwa, methylarsenicals in the hypolimnion did not directly result from the in situ activity of photosynthesis, since the transparency was at 1.0-2.4m and Chlorophyll *a* was almost absent below the depth of 6m [65].

### 2.2.5 Effects of Freshwater Animals

Freshwater animals are able to convert dimethylarsenic to trimethylarsenic compounds [87,88]. In laboratory studies, freshwater fish were able to accumulate and transform As when exposed to water containing 10 mg/L $As^{V}$ for a duration of 7 days [88]. $As^{III}$, $As^{V}$, mono-, di-,

and tri- methyl arsenic compounds were detected in eight tissues of the freshwater fish *Tilapia mossambica* and most tissues contained a large proportion of methylated As as trimethylated As (22-67%). In another laboratory study, freshwater fish and marsh snails also contained higher amounts of trimethylarsenic than dimethylarsenic compounds [87].

### 2.2.6 Microorganisms in Sediments

Methylated As species have been detected in the sediment interstitial water of freshwater which could be the result of detritus degradation and/or the results of in situ bacterial methylation [28,65]. Mn-, Fe-, and sulfate-reducing bacteria from anaerobic lake sediments can methylate and demethylate As [89]. Bright et al. [89]found that the extent of methylation by sediment microorganisms and the proportion of different methylated species varied for different culture conditions. The biota between the epilimnion and hypolimnions of lakes may differ resulting in different proportions of methylarsenicals present [58].

### 2.2.7 Effects of pH and Temperature on Biomethylation

The pH of water may be a factor in the biomethylation of As. Arsenic biomethylation was measured at pH 6.5 and 8.0 but was drastically restricted at pH 5.0 [83]. Temperature may also have an impact on methylation. Significant increases in DMA and MMA occurred as the surface water temperature of Upper Mystic Lake warmed from 5 °C to 19 °C [70]. In the hypolimnion of Lake Biwa, $DMA^V$ concentration and temperature correlated linearly but $DMA^V$ concentration in surface water was not proportional with temperature [65].

### 2.2.8 Effects of Phosphate

Phosphate concentrations may affect the methylation process [81]. $As^V$ is chemically similar to phosphate and may take its place in biotic pathways. In laboratory experiments the phosphate concentration affected the $DMA^V$ production by *C. aciculare* [81]. $DMA^V$ production was enhanced when the phosphate/$As^V$ ratio decreased in the culture medium. However, some

studies have found that there is no clear relationship between the $As^V$ /phosphate ratio and methylated forms of As [58,66]. Anderson and Bruland [58] found no correlation between $As^V$/phosphate ratios and increased $DMA^V$ concentrations in the Davis Creek Reservoir, USA. The authors conclude that because $DMA^V$ does not react significantly with particles, increases in $DMA^V$ and decreases in phosphate may be due to the removal of phosphate by organic matter [58]. Crowley Lake, USA contains high phosphorus concentrations due to inputs from geothermal water. Methylated As did not contribute significantly to the total As concentration in any Crowley Lake water samples [59]. Bright et al. [85] also did not find any relationship between methylarsenic and phosphate in sediment cores. In Lake Biwa, the southern basin was more productive, however, the northern basin contained similar concentrations of methylarsenicals [66]. The large load of phosphorus in the southern basin may have decreased the As metabolism efficiency of phytoplankton [66]. In the summer months, more than 95% of the As in the epilimnion of the Crowley Lake reservoir was $As^V$ even though the waters were very productive during this time [59]. Some species of phytoplankton may be able to discriminate between phosphate and $As^V$ better than others [90].

### 2.2.9 Arsenothiols

It is generally believed that the As species detected by hydride generation are the oxy species $(CH_3)_xAsO(OH)_{3-x}$ (x=0-3) [65,66]. However, As/sulfur compounds might be expected to dominate in the reducing environments [3]. The presence of the thio analogue [i.e., oxythioarsenate, $H_3As^VO_3S$] in water from an As-rich, reducing environment has been demonstrated [91]. Bright et al. [85] detected MMA, DMA and TMA in the reduced environment of lake sediment porewater indicating the possible presence of arsenothiols in freshwater. Dimethylarsinothiols in sediment porewaters could be a result of exocellular production from $DMA^V$ in the presence of reducing conditions (and sulfides) and /or thiolic compounds [85].

$DMA^V$ could be produced during upward diffusion of porewater containing dimethylarsenothiols into a more oxic environment [85].

## 2.3 Estuaries

### 2.3.0 Observed Arsenic Speciation

The chemical composition of seawater varies slightly from area to area due to the addition of freshwater and evaporation. The proportions of As species will also vary with the extent of anthropogenic input and biological activities. In a well-mixed estuary, a salinity gradient occurs between the river and the estuary mouth. These can be complex areas in which dissolved and particulate materials are subjected to often quite rapid changes in chemical and physical environments. The most significant changes involve pH and salinity. If either of these changes significantly, it can induce precipitation of dissolved species or redissolution of material from the sediments.

In the Saguenay Fjord Estuary, Canada, dissolved As showed very low concentrations in the freshwaters of the Saguenay River (~0.03 μg/L) and higher concentrations in the marine waters (~1 μg/L ) [92]. $As^V$ was the only detectable As species in the Itchen estuary in southern England most of the year [93]. However, 30% of the total As(0.7-1.0 μg/L) was in the form of methylated species when the temperature was above 12°C and when productivity was at a maximum. In the river, $DMA^V$ was found only in May and June. In the Seine Estuary, France, mean $MMA^V$ concentrations measured in October 1993 (0.025 μg/L) and September 1994 (0.022 μg/L) were comparable, however, in February 1995 the $MMA^V$ concentration was below detection limits [94]. It should be noted that the detection limit of the technique used was 0.022 μg/L. DMA related to phytoplankton activity represents a large fraction of dissolved total As except in winter [94]. $As^{III}$ concentrations increased with temperature but were less than 0.07 μg/L everywhere in February [94]. Methylated species were not detected in the winter and

midsummer in the upper Humber Estuary [95]. The sum of methylarsenicals found in surface waters comprised 2-25% and 10-82% of the total dissolved As in Tosa Bay and Uranouchi Inlet, Japan, respectively [96].

During an estuarine algal bloom in the Patuxent River (subestuary), USA, $As^{V}$ was rapidly reduced to $As^{III}$ and methylated species [97]. The rates of $As^{V}$ reduction and the species produced vary depending on the phytoplankton species composition and the season and the phytoplankton species composition will vary depending on the location in the estuary. Arsenate shares many chemical characteristics with phosphate and hence in oxic marine and estuarine waters, depletions in phosphate in biologically productive surface waters are mirrored by depletions in $As^{V}$ [9]. However, phosphate depletion cannot be a necessary prerequisite for $As^{V}$ assimilation in saline water because in Southampton Water, United Kingdom (U.K.), phosphate concentration remained high throughout 1988, yet As reduction and methylation occurred [98].

The behavior of As varies during estuarine mixing [9]. In the Tamar Estuary, southwest England, dissolved inorganic As was particularly elevated in the higher salinity region [99]. Riedel [100] observed that $As^{V}$ rises to maximum values before salinity reaches a maximum, and falls off during the period of highest salinities. Dissolved inorganic As concentrations in the Humber Estuary, U.K., were inversely related to salinity [95]. Inorganic As was linearly and inversely related to salinity in the upper Humber Estuary but in the lower estuary dissolved inorganic As behaved conservatively and was directly related to salinity [95]. Those elements which are neither added to, nor removed from the dissolved phase during the mixing of freshwater and seawater in the estuary are described as behaving conservatively. This is normally reflected in the concentration of the dissolved component being linearly related to salinity. Increases in pH and salinity may lead to the flocculation of Fe oxides at the point of mixing and this can lead to decreases in the As flux to the oceans [3,9].

### 2.3.1 Sediment and Sediment Porewater

Inorganic As, MMA and DMA were observed in samples of sediment porewater (0.04-0.7 μg/L) collected from the Tamar Estuary [101]. Arsenic is released to porewaters of the Saguenay Fjord Estuary, Canada, from the degradation of organic matter [92]. Reduced $As^{III}$ was the predominant species in the suboxic/anoxic porewaters of the Saguenay Fjord Estuary and could have been released in this form before the reductive dissolution of the Fe oxyhydroxides if the Fe oxyhydroxides were more resistant to dissolution.

Both $Fe^{III}$ and $Mn^{IV}$ (manganese) can oxidize $As^{III}$ as suggested by the following reactions [56]:

$$2Fe(OH)_3(am) + H_3AsO_3 + 3H^+ = 2Fe^{2+} + H_2AsO_4^- + 5H_2O$$
$$2Fe(OH)_3 + H_3AsO_3 + 4H^+ = 2Fe^{2+} + H_3AsO_4 + 5H_2O$$
$$MnO_2 + H_3AsO_3 + 2H^+ = Mn^{2+} + H_3AsO_4 + H_2O$$
$$MnO_2 + H_3AsO_3 + H^+ = Mn^{2+} + H_2AsO_4^- + H_2O$$
$$MnO_2 + H_3AsO_3 = Mn^{2-} + HAsO_4^{2-} + H_2O$$

Although both Fe and Mn oxides can oxidize $As^{III}$ to $As^V$ it is thought that Mn oxides are primarily responsible for the oxidation [56,71,92]. The methylation of As may prevent the adsorption to sediment and result in faster flushing from the estuary and less retention in the estuary [97]. The ratio of dissolved to particulate As distribution is controlled mainly by the Fe content of particles [94]. The adsorption of As on particulate matter occurs as a function of turbidity, salinity, pH, redox potential and biological activity [94]. As in suspended particulate matter in the Humber Estuary ranged from 7.4-76.4 μg/g [95].

## 2.4 Seawater

Total As concentrations in seawater are fairly stable at about 0.5-2 μg/L [62,90]. The major species in seawater are $As^V$ and $As^{III}$ and minor species are MMA and DMA (Table 2-1

and 2-2). Although arsenobetaine, arsenosugars, tetramethylarsonium, arsenocholine, and trimethylarsine oxide (TMAO) are found in marine life, they are not detected in surface seawater [80]. Uncharacterized As can average 25% of total As in seawater [80]. In marine sediments/porewater the major species are $As^{V}$, $As^{III}$, minor species are $MMA^{V}$, $DMA^{V}$ and trace species are TMAO and arsenobetaine [80]. Arsenosugars, TeMA (tetramethylarsonium ion), and arsenocholine have not been detected [80].

In oxygenated seawater, the $As^{V}/As^{III}$ ratios should be of the order of $10^{15}$-$10^{26}$ [102] whereas measured ratios of 0.1-250 have been found, largely supported by biological transformations [3]. Light only penetrates to about 200 m in oceans limiting photosynthesis to a relatively small upper layer of water. $As^{V}$ was the dominant species in both the East Indian and Antarctic Oceans surface water representing 52% and 97% respectively [90]. $As^{III}$ accounts for 27% and 0.2% in those regions. Fractions of MMA and DMA were 4% and 17% in east Indian and 0.8% and 2% in Antarctic waters. The surface waters of the Antarctic were more productive than the surface waters of the East Indian Ocean, but the MMA and DMA concentrations in the Antarctic surface were less than the east Indian Ocean. At sampling stations in the Pacific Ocean, inorganic As concentrations were low at the surface and deep/bottom zones and MMA and DMA were observed throughout the water column in the north western and equatorial regions [103]. Both $MMA^{V}$ and $DMA^{V}$ displayed maximum concentrations in surface water and abruptly dropped with depth from 0-200 m [104].

In the coastal waters of Tosa Bay (Pacific Ocean), $As^{V}$ was the dominant As species all year and slightly increased with depth, while the maxima of $As^{III}$ and $DMA^{III+V}$ were observed in surface waters [96]. In the Uranouchi inlet, the concentrations of the trivalent methylarsenic species $MMA^{III}$ and $DMA^{III}$ were low compared with those of the pentavalent species in most waters however, $MMA^{III}$ showed a marked increase approximately 0.004 $\mu$g/L from March to

May 1995, when $MMA^{III}$ was more abundant than $MMA^{V}$ [96]. The maximum concentration of $DMA^{III}$ was less than one tenth of that of $MMA^{III}$ and the sum of $MMA^{III}$ and $DMA^{III}$ lay within 18% of the sum of the methylarsenicals [96]. The concentrations of inorganic As increased with depth to maximum concentrations at a depth of 2000 m and then slowly decreased to minimum concentrations at a depth of 5000 m [104]. In the Atlantic Ocean, the As results were similar to those in other oceans, with moderate surface depletion, deep-water enrichment, a predominance of $As^{V}$ (>85%) and methylated As species and $As^{III}$ in surface waters [105].

### 2.4.0 Biological Transformation of Arsenic in Seawater

In marine systems, As can be transformed by bacteria, algae and other marine organisms [80,106,107]. Bacteria can oxidize $As^{III}$. Scudlark and Johnson [108] found that abiotic oxidation proceeds at a slow rate, however, in the presence of certain aquatic bacteria, the oxidation is rapid and the $As^{III}$ concentration decreases exponentially with time. Arsenosugars in algae and arsenobetaine in animals, are believed to be released to the sea at some point, as a consequence of grazing or predation by animals or the aging of the organism [109]. Though these As species have not been detected in seawater, there is increasing evidence that they may exist. In laboratory studies, the blue mussel *Mytilus edulis* was able to accumulate and convert arsenobetaine and arsenocholine to trimethylarsine oxide [110,111]. The plant *Fucus gardneri* was able to convert arsenate to $As^{III}$ and $DMA^{V}$ after exposure in water [112]. MMA was not detected. There was an increase in one arsenosugar but it was accompanied by a decrease in another arsenosugar so there was no conclusive evidence that arsenosugars were produced by *Fucus gardneri* [112]. In laboratory experiments, arsenobetaine and arsenocholine were completely degraded by microorganisms in seawater [109]. Arsenobetaine was transformed within hours initially to dimethylarsinoylacetate and then to DMA. Arsenocholine behaved

similarly but at a slower rate [109]. The rapidity of the degradation processes offers an explanation for the apparent absence of arsenobetaine in natural waters.

Organisms in marine sediments can also degrade arsenobetaine to inorganic As via TMAO under aerobic conditions [113]. In laboratory experiments, arsenobetaine-containing growth media were incubated with suspended substances as a source of marine microorganisms [114]. The mixture was able to degrade arsenobetaine to inorganic As, TMAO and $DMA^V$, suggesting the microbial degradation of arsenobetaine in the water column [114]. Laboratory studies have shown that microorganisms present in both natural marine sediments and sediments contaminated with mine-tailings are capable of methylating As under aerobic and anaerobic conditions [115]. Reimer [115] showed that the actual proportion of ethylated species was not dependent on the organic content of the sediments or the level of As concentration.

### 2.4.1 Uncharacterized Arsenic Species

In addition to the well-characterized As species discussed above in estuaries and seawater, there are also reports of unidentified (uncharacterized) As species in water [80,85,116-120]. After UV-irradiation of surface water from Uranouchi Inlet, the inorganic and dimethylarsenic concentrations detected with hydride generation rapidly increased [116]. The UV-labile As fractions comprised 15-45% and 4-26% of the total As in Uranouchi Inlet and Lake Biwa, respectively. UV-labile fraction is the increment in measurable As concentration before and after the 2.5h of UV irradiation. Between filtered (0.45 $\mu$m) and unfiltered samples, the difference in the uncharacterized fraction was significant compared with that of inorganic and methylarsenicals [116]. It is likely that the uncharacterized As captured on the 0.45 $\mu$m filter was derived from the organoarsenicals in biological organic detritus [116]. In sediment porewater, there was an increase of 18-420% in total dissolved As concentration observed after irradiation [85]. Michel et al. [120] reported a difference between the sum of known As species and total

As of 13% in the euphotic layer of an estuary. These studies suggest that substantial amounts of As remain to be characterized.

## 2.5 Treatment Options

Treatment options will depend on many factors, including the oxidation state of As and the concentration and species in source water [45,55]. $As^{V}$ is removed more easily than $As^{III}$ [55,121]. There are many different treatment options for the removal of As from groundwater. Most recently, modified chitosan beads, nanofiltration, zerovalent Fe filings, Fe-sulphide minerals (pyrite and pyrrhotite), aluminum-based coagulation, $Fe^{III}$-chelated iminodiacetate resins and various adsorbents have been used to remove arsenite and arsenate from groundwater [55,121-130].

Another possibility is to oxidize $As^{III}$ to $As^{V}$ before removal [56,131]. Kim & Nriagu [56] have attempted to oxidize $As^{III}$ in natural waters using ozone, air and oxygen. The presence of Fe and/or Mn will accelerate the oxidative removal of As. Clay minerals contain Fe oxides and are commonly present in the subsurface environment and are very effective at adsorbing $As^{V}$ than $As^{III}$ [132]. Dissolved Fe will precipitate as Fe oxyhydroxide under oxidizing conditions [24]. The oxyhydroxide scavenges As from solution. Therefore, it is possible that simple aeration of anoxic Bangladesh groundwater, followed by settling, should remove a considerable amount of As from solution [24]. Hug et al. [131] found that dissolved oxygen and micromolar hydrogen peroxide did not oxidize $As^{III}$ on a time scale of hours. In solutions containing 0.06-5 mg/L $Fe^{II,III}$, over 90% of $As^{III}$ could be oxidized photochemically within 2-3 h by illumination with 90 $W/m^2$. $Fe^{III}$ citrate complexes accelerated $As^{III}$ oxidation. Recently, the removal of $As^{III}$ and $As^{V}$ was performed using low cost ferruginous manganese ore and no pretreatment or preoxidation was necessary [133]. The ferruginous manganese ore was successfully used for the removal of As from six real groundwater samples [133]. Nanofiltration removed over 95% of

$As^{V}$ and more than 75% of $As^{III}$ in laboratory studies without any chemical additives [124]. However, $As^{III}$ could not be removed by rapid sand filtration system without pre-oxidation of $As^{III}$ to $As^{V}$ [124]. Source water composition also did not affect the removal of $As^{III}$ and $As^{V}$ by nanofiltration [124].

## 2.6 Concluding Remarks

High levels of As in aquatic systems can pose a serious hazard to the health of humans and the environment. To predict the potential toxicity to an aquatic system, As species distribution and the biogeochemical changes that will affect As speciation must be considered. The As species that are present in aquatic systems determine its toxicity and mobility. The measured levels of a particular chemical species in a water column represent the complex balance between production, chemical and microbial transformation and physical dispersal. It is necessary to not only understand the nature of the As species that are formed but also how they may be released or mobilized into the water.

Uncharacterized As species found in water samples and levels of particulate As should be focal points of further research on the biogeochemical processes of As cycling in the aquatic environment. These species may offer important details regarding the As speciation in natural waters and biological production in organisms. Understanding As speciation in water will contribute to more effective approaches to the removal of As.

**Table 2-1: Inorganic Arsenic Species Detected in Water[a]**

| | $As^{III}$ | $As^{V}$ | Refs. |
|---|---|---|---|
| **GROUNDWATER** | | | |
| Lead-Zinc Mine, Coeur d'Alene, Idaho, USA | 0.1-42.3 | N.A. | [134] |
| | 0.1-1336.1[b] | | [134] |
| South-west United States | <5 | 21-120 | [135] |
| Beaver Area, Utah, USA (Irrigation well water) | <1-54 | 3-18 | [48] |
| Saltspring, Utah, USA (one sample) | 1400 | 1180 | [48] |
| Colorado, USA (Acid mine water) | 4-13 | 1-2 | [48] |
| Bowen Island, British Columbia, Canada | N.D.-220 | N.D.-477.7 | [136] |
| La Pampa, Argentina | <3-105 | N.A. | [15] |
| | <4-5300[b] | | |
| Six Districts in West Bengal, India | 10-2600 | 16-1100 | [137] |
| West Bengal, India (Tube wells) Acidified (unacidified) | 6.8-501.7 | 7.7-184.5 | [138] |
| Purbasthali (Burdwan), India | Present in 1 | N.D.-133.6 | [4] |
| Bangladesh (Tubewell for drinking) | 30-1200[b] | | [20] |
| Bangladesh (Deep tubewell for drinking) | 50-80[b] | | [20] |
| Bangladesh (Deep tubewell for irrigation) | 30-200[b] | | [20] |
| Bangladesh | N.D. - >500 | N.A. | [22] |
| Bangladesh (Irrigation Well) | 88 | N.A. | [139] |
| | 96.9[b] | | |
| Bangladesh (Public Well) | 153 | N.A. | [139] |
| | 211[b] | | |
| Bangladesh (Domestic Wells) | 0.7-812 | N.A. | [139] |
| | 2.3-846[b] | | |
| Taiwan (Pu-Tai) endemic area | 285-683 | 33-362 | [32,140] |
| | (462±129) | (177±109) | |
| Taiwan (I-Lan) comparison area | 537-637 | 24-67 | [140] |
| | (572±42) | (38±18) | |
| Taiwan (Hsin-Chiu) control area | <3 | <12 | [140] |
| Taiwan (Pu-Tai) | ~20-720[b] | | [141] |
| Taiwan (Fushing) | 70.2±2.6 | 870±26 | [142] |
| Taiwan (Chiuying) | 51.6±1.8 | 601±22 | [142] |

| Table 2-1: continued | $As^{III}$ | $As^{V}$ | Refs. |
|---|---|---|---|
| Region Lagunera, northern Mexico | Trace-217 | 4-604 | [54] |
| Fukuoka Prefecture, Japan | 15-70 | 11-220 | [53] |
| Kelheim, Lower Bavaria, Germany[c] | N.D.-176.3 | N.D.-147.7 | [52] |
| **RIVERS** | | | |
| Hillsborough River, Tampa, Florida, USA | N.D. | 0.25±0.01 | [63] |
| Withlacoochee River, Tampa, Florida, USA | N.D. | 0.16±0.01 | [63] |
| Tamiami Canal, Florida, USA | 0.47 | 0.07 | [62] |
| Colorado River, Parker, Arizona, USA | 0.11 | 1.95 | [62] |
| Nine rivers in California, USA | 0.02-1.3 | 0.07-42.5 | [62] |
| Four rivers in California, USA | 0.7-7.4[b] | | [58] |
| Colorado River Slough, near Topock, California | 0.08 | 2.25 | [143] |
| North Saskatchewan River, Canada | 0.21±0.08 | 0.32±0.01 | [144] |
| Haya-kawa River, Japan | 28[b] | | [87] |
| River in Taiwan (Erhjin) | 2.95±3.52 | 4.59±1.31 | [142] |
| River in Taiwan (Tsengwen) | 0.12±0.06 | 2.57±1.17 | [142] |
| **LAKES, PONDS, RESERVOIRS** | | | |
| Mono Lake, California, USA (Highly alkaline lake) | 17250[b] | | [58] |
| Pyramid Lake, California, USA | 97.5[b] | | [58] |
| Six Lakes in California, USA | 0.3-11.2[b] | | [58] |
| Davis Creek Reservoir (filtered samples), California, USA | Trace-1.2 | 0.01-1.5 | [58] |
| Davis Creek Reservoir (unfiltered samples), California, USA | 0.8-2.6[b] | | [58] |
| Elkhorn Slough, California, USA | 1.1[b] | | [58] |
| Donner Lake N. Shore, California, USA | 0.06 | 0.07 | [62] |
| Saddleback Lake S. End, California, USA | 0.05 | 0.02 | [62] |
| Squaw Lake (surface), California, USA | 0.87 | 2.76 | [62] |
| Squaw Lake (2m depth), California, USA | 0.53 | 2.96 | [62] |
| Senator Wash Reservoir, California, USA | 0.58 | 2.47 | [62] |
| Lake Echols, Tampa, Florida, USA | 2.74±0.01 | 0.41±0.01 | [63] |
| Lake Magdalene, Tampa, Florida, USA | 0.89±0.01 | 0.49±0.01 | [63] |
| Remote Pond, Withlacoochee Forest, Tampa, Florida, USA | N.D. | 0.32±0.01 | [63] |
| University Research Pond, Tampa, Florida, USA | 0.79±0.01 | 0.96±0.01 | [63] |

| Table 2-1: continued | $As^{III}$ | $As^{V}$ | Refs. |
|---|---|---|---|
| **LAKES, PONDS, RESERVOIRS continued:** | | | |
| Coot Bay Pond, Everglades, Florida, USA | 0.81 | 1.27 | [62] |
| Paurotis Pond, Everglades, Florida, USA | 0.04 | 0.02 | [62] |
| Lake Washington, Seattle, USA | 40% of TDA | 60% of TDA | [145] |
| Lake Washington interstitial water, Seattle, USA (one sample) | 55% of TDA | N.D. | [146] |
| SubArctic Lakes[c] (pH 1) Yellowknife, NWT, Canada | N.A. | 0.7-520 | [85] |
| SubArctic Lakes[c] (pH 6) Yellowknife, NWT, Canada | 0-22 | N.A. | [85] |
| Lake Biwa, Japan | <0.2 | <1.9 | [65] |
| Lake in Taiwan (Nanjen Hu) | 0.05±0.00 | 1.67±0.07 | [142] |
| Lake Pavin, France (measurements at different depths) | 0-8.25 | 0.28-4.4 | [67] |
| **SEAWATER** | | | |
| Pacific Ocean (< 100m) | 1.1-1.6[b] | | [103,147,148] |
| Pacific Ocean, SE Taiwan | 0.05±0.02 | 1.28±0.24 | [142] |
| Western Atlantic Ocean (Stn.10) - Surface | ~0.3[b] | | [105] |
| Western Atlantic Ocean (Stn.10) - Deep Water (2200-3300m) | 1.5±0.1[b] | | [105] |
| Western Atlantic Ocean (Stn.10) - Bottom Water (3950-4460 m) | 1.5±0.03[b] | | [105] |
| Western Atlantic Ocean (Stn.10) – 80m deep mixed layer (maximum) | 0.03 | N.D. | [105] |
| Western Atlantic Ocean (Stn.10) – 700m to bottom (maximum) | 0.007 | N.D. | [105] |
| Antarctic Ocean | 0.003 | 1.0 | [90] |
| East Indian Ocean | 0.2 | 0.4 | [90] |
| North Indian Ocean | 0.2 | 0.5 | [90] |
| Baltic Sea | N.D.-0.92 | N.D.-1.01 | [149] |
| Southern North Sea (over several months) | 0.1-1.5[b] | | [146] |
| China Sea | 0.2 | 0.3 | [90] |
| Indonesian Archipelago | 0.2 | 0.4 | [90] |
| **ESTUARIES & COASTAL WATERS** | | | |
| Scripps Pier, La Jolla, California, USA | 0.01-0.03 | 1.70-1.75 | [143] |
| San Diego Trough, California, USA (surface – 100m below surface) | 0.01-0.06 | 1.32-1.67 | [143] |
| Suisun Bay, California, USA | 1.5[b] | | [58] |
| Southern California Bight (varying depths and locations) | N.D.-0.87 | 0.16-1.45 | [62] |

| Table 2-1: continued | $As^{III}$ | $As^{V}$ | Refs. |
|---|---|---|---|
| **ESTUARIES & COASTAL WATERS continued** | | | |
| Tidal Flat, Tampa, Florida, USA | 0.6±0.01 | 1.3±0.01 | [63] |
| Bay, Causeway, Tampa, Florida, USA | 0.1±0.01 | 1.4±0.01 | [63] |
| McKay Bay, Tampa, Florida, USA | 0.06±0.01 | 0.3±0.01 | [63] |
| Chesapeake Bay[c], Maryland, USA | N.D.-0.24 | 0.13-1.02 | [150] |
| Patuxent River Estuary, Maryland, USA (over two years) | 0.1-0.2 | 0.1-1.1 | [100] |
| Saanich Inlet, Vancouver, British Columbia, Canada (oxic stations) | 0.07-0.19 | 0.77-2.51 | [151] |
| Saanich Inlet, Vancouver, British Columbia, Canada (anoxic stations) | 0.07-1.91 | N.D.-2.20 | [151] |
| Hastings Arm[c] porewaters, British Columbia, Canada | 0.80-11.5 | 2.0-12.1 | [152] |
| Alice Arm[c] porewaters, British Columbia, Canada | 2.9-28.8 | 2.3-28.8 | [152] |
| Quatsino Sound[c] porewaters (One Station), British Columbia, Canada | Not reported | <3-10.5 | [152] |
| Holberg Inlet[c] porewaters (One Station), British Columbia, Canada | Not reported | 1.5-<13.5 | [152] |
| Rupert Inlet[c] porewaters (Two Stations), British Columbia, Canada | Not reported | <1.5-9.0 | [152] |
| Surface Waters of the Beaulieu Estuary, Hampshire, U.K. | <0.02-0.40 | N.A. | [153] |
| | 0.17-1.20[b] | | [153] |
| Deep Waters of the Beaulieu Estuary, Hampshire, U.K. | 0.43-1.07[b] | | [153] |
| Tamar Estuary[c], South-west England (primarily $As^{V}$) | ~2.7[b] | | [99] |
| Tamar Estuary[c] (porewaters), South-west England | ~29.6[b] | | [99] |
| Tamar Estuary[c] (porewaters), South-west England | 5-60[b] | | [101] |
| Southampton Water, U.K. | 0.03-0.1 | N.A. | [93] |
| Humber Estuary[c], U.K. (over four seasons) | 0.7-2.3[b] | | [95] |
| Thames Estuary and Plume[c], U.K. (Feb.1989) | 3.3±0.9 | N.A. | [146] |
| Thames Estuary and Plume[c], U.K. (July 1990) | 2.1±1.0[b] | | [146] |
| Seine Estuary, France (over several months) | N.D.-1.2 | 0.4-2.1 | [94] |
| Continental Shelf off the Gironde Estuary, France | 0.01-0.3 | 0.8-1.5 | [120] |
| Tagus Estuary[c], Atlantic coast of Europe | 2.8-14.7[b] | | [154] |
| Schelde Estuary[c], central Europe | 0.06-0.4 | 1.8-4.8 | [155] |
| Schelde Watershed[c], central Europe | 0.003-8.2 | 0.9-27.7 | [155] |
| Coastal water in Taiwan (Erhjin) | 0.06±0.04 | 0.88±0.25 | [142] |
| Coastal waters in Taiwan (Tsengwen) | 0.03±0.01 | 0.62±0.05 | [142] |
| **OTHER** | | | |
| Rainwater, Washington, USA | 35% of TDA | 65% of TDA | [145] |

| Table 2-1: continued | $As^{III}$ | $As^{V}$ | Refs. |
|---|---|---|---|
| **OTHER continued** | | | |
| Rainwater, La Jolla, California, USA | <0.002 | 0.09-0.18 | [143] |
| Hot Creek Gorge, Eastern Sierra Nevada, USA | 0.61±0.20 | N.D. | [71] |
| North Drainage Channel-Twin Butte Vista Hot Spring, Yellowstone National Park, USA | 610-1900 | 600-1900 | [60] |
| Bottled mineral water (23 brands)($As^{V}$ predominate in 19 and $As^{III}$ predominate in 4) | 0.05-220[b] | | [156] |
| Bottled Slovene mineral water | <1 | <1-60.6 | [157] |
| Bottled Water (carbonated) | 1.6±0.1 | 7.5±0.3 | [158] |
| Bottled mineral Water (Vichy) | 180±5[b] (90% present as $As^{V}$) | | [159] |

N.D. – not detected
N.A. – not analyzed separately (Only $As^{III}$ and/or Total dissolved As reported)
TDA – Total dissolved As
[a]All concentrations in µg/L
[b]The sum of $As^{III}$+$As^{V}$
[c]Anthropogenic contamination

**Table 2-2: Organic Arsenic Species Detected in Water[a]**

| | MMA | DMA | TMA | Refs. |
|---|---|---|---|---|
| **GROUNDWATER** | | | | |
| Taiwan (Pu-Tai) | ~0.5-4.2 | ~2.0-6.9 | ~3.3-5.1 | [141] |
| Region Lagunera, northern Mexico | <3 | Trace-20 | | [54] |
| West Bengal, India | N.D.-2.1 | N.D.-0.7 | | [138] |
| **RIVERS** | | | | |
| Withlacoochee River, Tampa, Florida, USA | 0.06±0.01 | 0.3±0.01 | | [63] |
| Tamiami Canal, Florida, USA | <0.005 | 0.05 | | [62] |
| Colorado River, Parker, Arizona, USA | 0.06 | 0.05 | | [62] |
| Nine rivers in California, USA | <0.007-0.56 | <0.007-0.31 | | [62] |
| Colorado River Slough, near Topock, California | 0.13 | 0.31 | | [143] |
| Haya-kawa River, Japan | N.D. | N.D. | 2 | [87] |
| **LAKES, PONDS, RESERVOIRS** | | | | |
| Pyramid Lake, California, USA | N.D. | 1.1 | | [58] |
| Six Lakes in California, USA | N.D.-0.6 | 0.03-2.4 | | [58] |
| Davis Creek Reservoir (filtered samples), California, USA | 0.18-0.3 | 0.03-0.9 | | [58] |
| Davis Creek Reservoir (unfiltered samples), California, USA | 0.22-0.3 | N.D.-0.8 | | [58] |
| Elkhorn Slough, California, USA | 0.07 | 0.2 | | [58] |
| Donner Lake N. Shore, California, USA | <0.008 | 0.003 | | [62] |
| Saddleback Lake S. End, California, USA | <0.002 | 0.006 | | [62] |
| Squaw Lake (surface), California, USA | 0.022 | 0.052 | | [62] |
| Squaw Lake (2m depth), California, USA | 0.020 | 0.11 | | [62] |
| Senator Wash Reservoir, California, USA | 0.014 | 0.006 | | [62] |
| Lake Echols, Tampa, Florida, USA | 0.11±0.01 | 0.32±0.01 | | [63] |
| Lake Magdalene, Tampa, Florida, USA | 0.22±0.01 | 0.15±0.01 | | [63] |
| Remote Pond, Withlacoochee Forest, Tampa, Florida, USA | 0.12±0.01 | 0.62±0.01 | | [63] |
| University Research Pond, Tampa, Florida, USA | 0.05±0.01 | 0.15±0.01 | | [63] |
| Coot Bay Pond, Everglades, Florida, USA | <0.01 | 0.32 | | [62] |

| Table 2-2: continued | MMA | DMA | TMA | Refs. |
|---|---|---|---|---|
| **LAKES, PONDS, RESERVOIRS continued** | | | | |
| Paurotis Pond, Everglades, Florida, USA | <0.005 | 0.03 | | [62] |
| Lake Washington, Seattle, USA | N.D. | 0.05 | | [145] |
| Lake Washington interstitial water, Seattle, USA (one sample) | N.D. | 1 | | [145] |
| SubArctic Lakes[c] (pH 1) Yellowknife, NWT, Canada | N.D.-0.5 | N.D.-0.7 | N.D.-0.2 | [85] |
| SubArctic Lakes[c] (pH 6) Yellowknife, NWT, Canada | N.D.-0.04 | N.D. | N.D. | [85] |
| Lake Biwa, Japan | <0.05 | <0.76 | | [65] |
| | <0.01 ($MMA^{III}$) | <0.01($DMA^{III}$) | | |
| Lake Pavin, France (measurements at different depths) | Not quantified | Not quantified | | [67] |
| **SEAWATER** | | | | |
| Pacific Ocean (< 100m) | 0.009-0.02 | 0.02-0.2 | | [103,148] |
| Western Atlantic Ocean – Upper 200 m | 0.007 | 0.05 | | [105] |
| Antarctic Ocean | 0.007 | 0.02 | | [90] |
| East Indian Ocean | 0.03 | 0.05 | | [90] |
| North Indian Ocean | 0.03 | 0.2 | | [90] |
| Baltic Sea | N.D.-0.03 | N.D.0.52 | | [149] |
| Southern North Sea (over several months) | 0-0.1 | 0.05-0.3 | | [146] |
| China Sea | 0.02 | 0.08 | | [90] |
| Indonesian Archipelago | 0.03 | 0.09 | | [90] |
| **ESTUARIES & COASTAL WATERS** | | | | |
| Scripps Pier, La Jolla, California, USA | 0.01-0.02 | 0.12 | | [143] |
| San Diego Trough, California, USA (surface – 100m below surface) | 0.003-0.005 | 0.002-0.21 | | [143] |
| Suisun Bay, California, USA | 0.1 | 0.07 | | [58] |
| Southern California Bight (varying depths and locations) | <0.002-0.031 | 0.01-0.26 | | [62] |
| Tidal Flat, Tampa, Florida, USA | 0.08 | 0.3 | | [63] |
| Bay, Causeway, Tampa, Florida, USA | N.D. | 0.2 | | [63] |
| McKay Bay, Tampa, Florida, USA | 0.07 | 1.0 | | [63] |
| Chesapeake Bay[c], Maryland, USA | N.D.-0.42 | N.D.-0.34 | | [150] |
| Patuxent River Estuary, Maryland, USA (over two years)(max. values) | <0.3 | 0.2-0.6 | | [100] |

| Table 2-2: continued | MMA | DMA | TMA | Refs. |
|---|---|---|---|---|
| **ESTUARIES & COASTAL WATERS continued** | | | | |
| Hastings Arm[c] porewaters, British Columbia, Canada | <0.03 | 0.09-0.23 | <0.22 (TMAO) | [152] |
| Alice Arm[c] porewaters, British Columbia, Canada | <0.47 | <0.19 | <0.41 (TMAO) | [152] |
| Quatsino Sound[c] porewaters (One Station), British Columbia, Canada | <0.18 | <0.22 | <0.70 (TMAO) | [152] |
| Holberg Inlet[c] porewaters (One Station), British Columbia, Canada | <0.04 | <0.04 | <0.27 (TMAO) | [152] |
| Rupert Inlet[c] porewaters (Two Stations), British Columbia, Canada | <0.33 | <0.24 | <0.25 (TMAO) | [152] |
| Surface Waters of the Beaulieu Estuary, Hampshire, U.K. | <0.02-0.32 | <0.02-0.44 | | [153] |
| Deep Waters of the Beaulieu Estuary, Hampshire, U.K. | 0.03-0.26 | 0.19-0.40 | | [153] |
| Tamar Estuary[c], South-west England | 0.2-0.5 | 0.02-1.3 | | [99] |
| Tamar Estuary[c] (porewaters), South-west England | 0.4 | 0.5 | | [99] |
| Tamar Estuary[c] (porewaters), South-west England | 0.04-0.7 | 0.1-0.5 | | [101] |
| Southampton Water, U.K. | 0.03-0.08 | 0.05-0.5 | | [93] |
| Humber Estuary[c], U.K. (over four seasons) | N.D.-0.02 | N.D.-0.2 | | [95] |
| Thames Estuary and Plume[c], U.K. (Feb.1989) | N.D. | N.D. | | [146] |
| Thames Estuary and Plume[c], U.K. (July 1990) | 0.036±0.016 | 0.138±0.127 | | [146] |
| Seine Estuary, France (over several months) | N.D.-0.05 | N.D.-0.3 | | [94] |
| Continental Shelf off the Gironde Estuary, France | N.D. | 0-0.1 | | [120] |
| Tagus Estuary[c], Atlantic coast of Europe | 0.01-0.06 | 0.07-0.2 | 0.01-0.04 | [154] |
| **OTHER** | | | | |
| Rainwater, La Jolla, California, USA | <0.002 | <0.002-0.024 | | [143] |

N.D. – not detected
[a]All concentrations in µg/L
[b]The sum of $As^{III}$+$As^{V}$
[c]Anthropogenic contamination

## 2.7 References


[1] A.H. Welch, M.S. Lico, J.L. Hughes, Ground Water 26 (1988) 333.

[2] J.F. Ferguson, J. Gavis, Wat. Res. 6 (1972) 1259.

[3] W.R. Cullen, K.J. Reimer, Chem. Rev. 89 (1989) 713.

[4] J.K. Nag, V. Balaram, R. Rubio, J. Alberti, A.K. Das, J. Trace Elem. Med. Biol. 10 (1996) 20.

[5] NRC, Arsenic in Drinking Water, National Academy Press, Washington, DC, 1999.

[6] W.M. Mok, C.M. Wai, in J.O. Nriagu (Editor), Arsenic in the Environment, Part I:Cycling and Characterization, John Wiley & Sons, Inc., 1994.

[7] S. Tamaki, W.T. Frankenberger, Rev. Environ. Contam. Toxicol. 124 (1992) 79.

[8] A.H. Welch, Ground water 38 (2000) 589.

[9] P.L. Smedley, D.G. Kinniburgh, Appl. Geochem. 17 (2002) 517.

[10] U.K. Chowdhury, B.K. Biswas, T.R. Chowdhury, G. Samanta, B.K. Mandal, G.C. Basu, C.R. Chanda, D. Lodh, K.C. Saha, S.K. Mukherjee, S. Roy, S. Kabir, Q. Quamruzzaman, D. Chakraborti, Environ. Health Perspect. 108 (2000) 393.

[11] U.K. Chowdhury, B.K. Biswas, G. Dhar, G. Samanta, B.K. Mandal, T.R. Chowdhury, D. Chakraborti, S. Kabir, S. Roy, in W.R. Chappell, C.O. Abernathy, R.L. Calderon (Editors), Arsenic Exposure and Health Effects, Elsevier, Amsterdam, 1999, p. 165.

[12] G. Samanta, T.R. Chowdhury, B.K. Mandal, B.K. Biswas, U.K. Chowdhury, G.C. Basu, C.R. Chanda, D. Lodh, D. Chakraborti, Microchem. J. 62 (1999) 174.

[13] Z.D. Luo, Y.M. Zhang, L. Ma, G.Y. Zhang, X. He, R. Wilson, D.M. Byrd, J.G. Griffiths, S. Lai, L. He, K. Grumski, S.H. Lamm, in C.O. Abernathy, R.L. Calderon, W.R. Chappell (Editors), Arsenic Exposure and Health Effects, Chapman & Hall, London, 1999, p. 55.

[14] D. Chakraborti, M.M. Rahman, K. Paul, U.K. Chowdhury, M.K. Sengupta, D. Lodh, C.R. Chanda, K.C. Saha, S.C. Mukherjee, Talanta 58 (2002) 3.

[15] P.L. Smedley, H.B. Nicolli, D.M.J. Macdonald, A.J. Barros, J.O. Tullio, Appl. Geochem. 17 (2002) 259.

[16] N.C. Woo, M.J. Choi, Environ. Geol. 40 (2001) 305.

[17] M.J. Kim, J. Nriagu, S. Haack, Environ. Sci. Technol. 34 (2000) 3094.

[18] C. Roussel, H. Bril, A. Fernandez, J. Environ. Qual. 29 (2000) 182.

[19] M.A. Armienta, G. Villasenor, R. Rodriguez, L.K. Ongley, H. Mango, Environ. Geol. 40 (2001) 571.

[20] K. Tanabe, H. Yokota, H. Hironaka, S. Tsushima, Y. Kubota, Appl. Organometal. Chem. 15 (2001) 241.

[21] R.T. Nickson, J.M. McArthur, P. Ravenscroft, W.G. Burgess, K.M. Ahmed, Appl. Geochem. 15 (2000) 403.

[22] S.B. Rasul, A.K.M. Munir, Z.A. Hossain, A.H. Khan, M. Alauddin, A. Hussam, Talanta 58 (2002) 33.

[23] N.E. Korte, Environ. Geol. Water. Sci. 18 (1991) 137.

[24] R. Nickson, J. MCarthur, W. Burgess, K.M. Ahmed, P. Ravenscroft, M. Rahmann, Nature 395 (1998) 338.

[25] S.K. Acharyya, S. Lahiri, B.C. Raymahashay, A. Bhowmik, Environ. Geol. 39 (2000) 1127.

[26] H.W. Langner, W.P. Inskeep, Environ. Sci. Technol. 34 (2000) 3131.

[27] H. Mccreadie, D.W. Blowes, C.J. Ptacek, J.L. Jambor, Environ. Sci. Technol. 34 (2000) 3159.

[28] X. Meng, C. Jing, G.P. Korfiatis, in Y. Cai, O.C. Braids (Editors), Biogeochemistry of Environmentally Important Trace Elements, American Chemical Society, Washington, DC, 2003, p. 70.

[29] C. Su, R.W. Puls, Environ. Sci. Technol. 35 (2001) 4562.

[30] C.A.J. Appelo, M.J.J. Van Der Weiden, C. Tournassat, L. Charlet, Environ. Sci. Technol. 36 (2002) 3096.

[31] J.G. Hering, V.Q. Chiu, J. Environ. Eng. (2000) 471.

[32] S.L. Chen, S.R. Dzeng, M.H. Yang, K.H. Chiu, G.M. Shieh, C.M. Wai, Environ. Sci. Technol. 28 (1994) 877.

[33] A.J. Bednar, J.R. Garbarino, J.F. Ranville, T.R. Wildeman, Environ. Sci. Technol. 36 (2002) 2213.

[34] J.A. Cherry, A.U. Shaikh, D.E. Tallman, R.V. Nicholson, J Hydrol. 43 (1979) 373.

[35] X.C. Le, S. Yalcin, M. Ma, Environ. Sci. Technol. 34 (2000) 2342.

[36] M.J. Kim, Bull. Environ. Contam. Toxicol. 67 (2001) 46.

[37] M. Raessler, B. Michalke, P. Schramel, S. Schulte-Hostede, A. Kettrup, Intern. J. Environ. Anal. Chem. 72 (1998) 195.

[38] A.F. Roig-Navarro, Y. Martinez-Bravo, F.J. Lopez, F. Hernandez, J. Chromatogr. A 912 (2001) 319.

[39] M. Edwards, S. Patel, L. McNeill, H.W. Chen, M.M. Frey, A.D. Eaton, R.C. Antweiler, H.E. Taylor, J. Am. Water Works. Assoc. 90 (1998) 103.

[40] G.E.M. Hall, J.C. Pelchat, G. Gauthier, J. Anal. At. Spectrom. 14 (1999) 205.

[41] A. Palacios, M. Gomez, C. Camara, M.A. Lopez, Anal. Chim. Acta 340 (1997) 209.

[42] T. Lindemann, A. Prange, W. Dannecker, B. Neidhart, Fres. J. Anal. Chem. 368 (2000) 214.

[43] B. Daus, J. Mattusch, R. Wennrich, H. Weiss, Talanta 58 (2002) 57.

[44] M. Borho, P. Wilderer, J. Wat. SRT-Aqua 46 (1997) 138.

[45] P. Gallagher, C.A. Schwegel, X. Wei, J.T. Creed, J. Environ. Monit. 3 (2001).

[46] Z. Gong, X. Lu, W.R. Cullen, X.C. Le, J. Anal. At. Spectrom. 16 (2001) 1409.

[47] Z. Jokai, J. Hegoczki, P. Fodor, Microchem. J. 59 (1998) 117.

[48] W.H. Ficklin, Talanta 30 (1983) 371.

[49] G.P. Miller, D.I. Norman, P.L. Frisch, Wat. Res. 34 (2000) 1397.

[50] R. Feeney, S.P. Kounaves, Anal. Chem. 72 (2000) 2222.

[51] D.G. Kinniburgh, W. Kosmus, Talanta 58 (2002) 165.

[52] M. Raessler, B. Michalke, S. Schulte-Hostede, A. Kettrup, Sci. Tot. Environ. 258 (2000) 171.

[53] H. Kondo, Y. Ishiguro, K. Ohno, M. Nagase, M. Toba, M. Takagi, Wat. Res. 33 (1999) 1967.

[54] L.M. Del Razo, M.A. Arellano, M.E. Cebrian, Environ. Pollut. 64 (1990) 143.

[55] H.W. Chen, M.M. Frey, D. Clifford, L.S. McNeill, M. Edwards, J. Am. Water Works. Assoc. 91 (1999) 74.

[56] M.J. Kim, J. Nriagu, Sci. Tot. Environ. 247 (2000) 71.

[57] B. Planer-Friedrich, M.A. Armienta, B.J. Merkel, Environ. Geol. 40 (2001) 1290.

[58] L.C.D. Anderson, K.W. Bruland, Environ. Sci. Technol. 25 (1991) 420.

[59] P.E. Kneebone, J.G. Hering, Environ. Sci. Technol. 34 (2000) 4307.

[60] T.M. Gihring, G.K. Druschel, R.B. Mccleskey, R.J. Hamers, J.F. Banfield, Environ. Sci. Technol. (2001) 3857.

[61] E. Buyuktuncel, S. Bektas, B. Salih, M.M. Evirgen, O. Genc, Fres. Envir. Bull. 6 (1997) 494.

[62] M.O. Andreae, Deep Sea Res. 25 (1978) 391.

[63] R.S. Braman, C.C. Foreback, Science 182 (1973) 1247.

[64] A.G. Howard, S.D.W. Comber, Appl. Organometal. Chem. 3 (1989) 509.

[65] H. Hasegawa, Appl. Organometal. Chem. 11 (1997) 305.

[66] Y. Sohrin, M. Matsui, M. Kawashima, M. Hojo, H. Hasegawa, Environ. Sci. Technol. 31 (1997) 2712.

[67] P. Seyler, J.M. Martin, Environ. Sci. Technol. 23 (1989) 1258.

[68] A. Kuhn, L. Sigg, Limnol. Oceanogr. 38 (1993) 1052.

[69] E.A. Crecelius, M.H. Bothner, R. Carpenter, Environ. Sci. Technol. 9 (1975) 325.

[70] A.C. Aurillo, R.P. Mason, H.F. Hemond, Environ. Sci. Technol. 28 (1994) 577.

[71] J.A. Wilkie, J.G. Hering, Environ. Sci. Technol. 32 (1998) 657.

[72] R.E. Macur, J.T. Wheeler, T.R. McDermott, W.P. Inskeep, Environ. Sci. Technol. asap (2001).

[73] D. Ahmann, L.R. Krumholz, D.R. Lovley, F.M.M. Morel, Environ. Sci. Technol. 31 (1997) 2923.

[74] D.E. Cummings, F. Caccavo, S. Fendorf, R.F. Rosenzweig, Environ. Sci. Technol. 33 (1999) 723.

[75] D.E. Cummings, A.W. March, B. Bostick, S. Spring, F. Caccavo, S. Fendorf, R.F. Rosenzweig, Appl. Environ. Microbiol. 66 (2000) 154.

[76] K.P. Raven, A. Jain, R.H. Loeppert, Environ. Sci. Technol. 32 (1998) 344.

[77] J.Y. Kim, A.P. Davis, K.W. Kim, Environ. Sci. Technol. 37 (2003) 189.

[78] A.D. Redman, D.L. Macalady, D. Ahmann, Environ. Sci. Technol. 36 (2002) 2889.

[79] C.Y. Chen, C.L. Folt, Environ. Sci. Technol. 34 (2000) 3878.

[80] K.A. Francesconi, J.S. Edmonds, Adv. Inorg. Chem. 44 (1997) 147.

[81] H. Hasegawa, Y. Sohrin, K. Seki, M. Sato, K. Norisuye, K. Naito, M. Matsui, Chemosphere 43 (2001) 265.

[82] M.J. La Force, C.M. Hansel, S. Fendorf, Environ. Sci. Technol. 34 (2000) 3937.

[83] A.A. Carbonell-Barrachina, A. Jugsujinda, F. Burlo, R.D. Delaune, W.H. Patrick Jr., Wat. Res. 34 (2000) 216.

[84] H.M. Spliethoff, R.P. Mason, H.F. Hemond, Environ. Sci. Technol. 29 (1995) 2157.

[85] D.A. Bright, M. Dodd, K.J. Reimer, Sci. Tot. Environ. 180 (1996) 165.

[86] A.R. Abdel-Moati, Wat. Air. Soil. Pollut. 51 (1990) 117.

[87] T. Kaise, M. Ogura, T. Nozaki, K. Saitoh, T. Sakurai, C. Matsubara, C. Watanabe, K. Hanaoka, Appl. Organometal. Chem. 11 (1997) 297.

[88] A.O. Suhendrayatna, N. Tsunenori, M. Shigeru, Appl. Organometal. Chem. 15 (2001) 566.

[89] D.A. Bright, S. Brock, W.R. Cullen, G.M. Hewitt, J. Jafaar, K.J. Reimer, Appl. Organometal. Chem. 8 (1994) 415.

[90] S.J. Santosa, S. Wada, S. Tanaka, Appl. Organometal. Chem. 8 (1994) 273.

[91] G. Schwedt, M. Rieckhoff, J. Chromatogr. A 736 (1996) 341.

[92] A. Mucci, L.F. Richard, M. Lucotte, C. Guignard, Aqua. Geochem. 6 (2000) 293.

[93] A.G. Howard, S.C. Apte, Appl. Organometal. Chem. 3 (1989) 499.

[94] P. Michel, J.F. Chiffoleau, B. Averty, D. Auger, E. Chartier, Cont. Shelf Res. 19 (1999) 2041.

[95] H.J. Kitts, G.E. Millward, A.W. Morris, L. Ebdon, Estuar. Coast Shelf Sci. 39 (1994) 157.

[96] H. Hasegawa, Appl. Organometal. Chem. 10 (1996) 733.

[97] J.G. Sanders, G.F. Riedel, Estuaries 16 (1993) 521.

[98] A.G. Howard, S.D.W. Comber, D. Kifle, E.E. Antai, D.A. Purdie, Estuar. Coast Shelf Sci. 40 (1995) 435.

[99] A.G. Howard, S.C. Apte, S.D.W. Comber, R.J. Morris, Estuar. Coast Shelf Sci. 27 (1988) 427.

[100] G.F. Riedel, Estuaries 16 (1993) 533.

[101] L. Ebdon, A.P. Walton, G.E. Millward, M. Whitfield, Appl. Organometal. Chem. 1 (1987) 427.

[102] M.O. Andreae, Limnol. Oceanogr. 24 (1979) 440.

[103] S.J. Santosa, H. Mokudai, M. Takahashi, S. Tanaka, Appl. Organometal. Chem. 10 (1996) 697.

[104] S.J. Santosa, S. Wada, H. Mokudai, S. Tanaka, Appl. Organometal. Chem. 11 (1997) 403.

[105] G.A. Cutter, L.S. Cutter, A.M. Featherstone, S.E. Lohrenz, Deep. Sea. Res. II 28 (2001) 2895.

[106] J.S. Edmonds, K.A. Francesconi, Experientia 43 (1987) 553.

[107] J.S. Edmonds, K.A. Francesconi, J.A. Hansen, Experientia 38 (1982) 643.

[108] J.R. Scudlark, D.L. Johnson, Estuar. Coast Shelf Sci. 14 (1982) 693.

[109] S. Khokiattiwong, W. Goessler, S.N. Pedersen, R. Cox, K.A. Francesconi, Appl. Organometal. Chem. 15 (2001) 481.

[110] J. Gailer, K.A. Francesconi, J.S. Edmonds, K.J. Irgolic, Appl. Organometal. Chem. 9 (1995) 341.

[111] W.R. Cullen, J.C. Nelson, Appl. Organometal. Chem. 7 (1993) 319.

[112] S.C.R. Granchinho, E. Polishchuk, W.R. Cullen, K.J. Reimer, Appl. Organometal. Chem. 15 (2001) 553.

[113] K. Hanaoka, S. Tagawa, T. Kaise, Hydrobiologia 235/236 (1992) 623.

[114] K. Hanaoka, H. Koga, S. Tagawa, T. Kaise, Comp. Biochem. Physiol. 101B (1992) 595.

[115] K.J. Reimer, Appl. Organometal. Chem. 3 (1989) 475.

[116] H. Hasegawa, M. Matsui, S. Okamura, M. Hojo, N. Iwasaki, Y. Sohrin, Appl. Organometal. Chem. 13 (1999) 113.

[117] R.E. Sturgeon, K.W.M. Siu, S.N. Willie, S.S. Berman, Analyst 114 (1989) 1393.

[118] A.M. de Bettencourt, M.O. Andreae, Appl. Organometal. Chem. 4 (1991) 111.

[119] A.M. de Bettencourt, M.H. Florencio, M.F.N. Duarte, M.L.R. Gomes, L.F.C. Vilas Boas, Appl. Organometal. Chem. 8 (1994) 43.

[120] P. Michel, B. Boutier, A. Herbland, B. Averty, L.F. Artigas, D. Auger, E. Chartier, Oceanol. Acta 21 (1997) 325.

[121] H. Jingtai, W.S. Fyfe, Chin. Sci. Bull. 45 (2000) 1430.

[122] C. Su, R.W. Puls, Environ. Sci. Technol. 35 (2001) 1487.

[123] J. Gregor, Wat. Res. 35 (2001) 1659.

[124] Y. Sato, M. Kang, T. Kamei, Y. Magara, Wat. Res. 36 (2002) 3371.

[125] L. Dambies, T. Vincent, E. Guibal, Wat. Res. 36 (2002) 3699.

[126] N. Melitas, J. Wang, M. Conklin, P. O'Day, J. Farrell, Environ. Sci. Technol. 36 (2002) 3188.

[127] D. Rau, A. Gonzalo, M. Valiente, React. Funct. Polymers 54 (2003) 85.

[128] C.A. Deliyanni, D.N. Bakoyannakis, A. Zouboulis, K.A. Matis, Chemosphere 50 (2003) 155.

[129] M.J. DeMarco, M.K. Sengupta, J.E. Greenleaf, Wat. Res. 37 (2003) 164.

[130] B. Van der Bruggen, C. Vandecasteele, Environ. Pollut. 122 (2003) 435.

[131] S.J. Hug, L. Canonica, M. Wegelin, D. Gechter, U.V. Gunten, Environ. Sci. Technol. 35 (2001) 2114.

[132] Z. Lin, R.W. Puls, Environ. Geol. 39 (2000) 753.

[133] S. Chakravarty, V. Dureja, S. Bhattacharyya, s. Maity, S. Bhattacharjee, Wat. Res. 36 (2002) 625.

[134] W.M. Mok, J.A. Riley, C.M. Wai, Wat. Res. 22 (1988) 769.

[135] F.N. Robertson, Env. Geochem. Health 11 (1989) 171.

[136] D.R. Boyle, R.J.W. Turner, G.E.M. Hall, Env. Geochem. and Health 20 (1998) 199.

[137] A. Chatterjee, D. Das, B.K. Mandal, T.R. Chowdhury, G. Samanta, D. Chakraborti, Analyst 120 (1995) 643.

[138] A. Shraim, N.C. Sekaran, C.D. Anuradha, S. Hirano, Appl. Organometal. Chem. 16 (2002) 202.

[139] P. Bhattacharya, G. Jacks, K.M. Ahmed, A.A. Khan, J. Routh, Bull. Env. Cont. Toxicol. 69 (2002) 538.

[140] S.L. Chen, S.J. Yeh, M.H. Yang, T.H. Lin, Biol. Trace Elem. Res. 48 (1995) 263.

[141] T.H. Lin, Y.L. Huang, M.Y. Wang, J. Toxicol. Environ. Health 53 (1998) 85.

[142] T.C. Hung, S.M. Liao, Toxicol. Environ. Chem. 56 (1996) 63.

[143] M.O. Andreae, Anal. Chem. 49 (1977) 820.

[144] S. Yalcin, X.C. Le, J. Environ. Monit. 3 (2001) 81.

[145] E.A. Crecelius, Limnol. Oceanogr. 20 (1975) 441.

[146] G.E. Millward, H.J. Kitts, S.D.W. Comber, L. Ebdon, A.G. Howard, Estuar. Coast Shelf Sci. 43 (1996) 1.

[147] J.G. Sanders, Chemosphere 3 (1979) 135.

[148] S.J. Santosa, H. Mokudai, S. Tanaka, J. Anal. At. Spectrom. 12 (1997) 409.

[149] M.O. Andreae, P.N. Froelich, Tellus 36B (1984) 101.

[150] J.G. Sanders, Mar. Chem. 17 (1985) 329.

[151] M.L. Peterson, R. Carpenter, Mar. Chem. 12 (1983) 295.

[152] J.J. Reimer, J.A.J. Thompson, Biogeochemistry 6 (1988) 211.

[153] A.G. Howard, M.H. Arbab-Zavar, S.C. Apte, Estuar. Coast Shelf Sci. 19 (1984) 493.

[154] A.M. de Bettencourt, Neth. J. Sea Res. 22 (1988) 205.

[155] M.O. Andreae, T.W. Andreae, Estuar. Coast Shelf Sci. 29 (1989) 421.

[156] J.G. Farmer, L.R. Johnson, Environ. Geochem. Health 7 (1985) 124.

[157] J.T. van Elteren, V. Stibilj, Z. Slejkovec, Wat. Res. 36 (2002) 2967.

[158] S. Yalcin, X.C. Le, Talanta 47 (1998) 787.

[159] C.T. Tye, S.J. Haswell, P. O'Neill, K.C.C. Bancroft, Anal. Chim. Acta 169 (1985) 195.

## Chapter 3. Speciation of Soluble Arsenic in Well Water using SPE Cartridges

### 3.0 Introduction

Arsenic is present in the environment and biological systems due to both natural and anthropogenic processes. Over two dozen inorganic and organic As compounds have been identified. In groundwater and wastewater, the soluble species of As are present as the inorganic forms of $As^{III}$ and $As^{V}$ [1,2]. Optimal removal methods from drinking water and wastewater will depend on the species of As present [3,4]. The species present will also determine whether any pretreatment is necessary before removal. $As^{V}$ is typically more easily removed than $As^{III}$ [4]. At the typical pH values of natural water (6.5-8.5), $As^{V}$ is present as an anionic species whereas $As^{III}$ is present as a neutral species. The negatively charged $As^{V}$ can be removed using a positively charged adsorbent. Consequently, if a significant percentage of the total soluble As is present as $As^{III}$, pretreatment such as oxidation may be necessary. In addition to removal and treatment processes, As speciation studies may help make more accurate assessments of environmental impact and health risks.

Efficient separation methods coupled to sensitive detectors are required to determine the levels of As species in water. The ideal method for determining soluble As species in groundwater and wastewater should be inexpensive, easy to use and relatively rapid. The coupling of chromatography with various sensitive detectors has lead to significant improvement in the detection of low levels of As species. There are three major HPLC systems. These are ion exchange, reversed phase ion pair and gel permeation [5]. Anion exchange is the most used separation technique because of the widely varying first $pK_a$ values of As species [5,6]. The first pKa of $As^{III}$ is 9.2 and the first pKa of $As^{V}$ is 2.2. The use of solid phase extraction cartridges (SPEC) is an efficient and rapid way of separating inorganic As species in water. These

cartridges are very inexpensive compared to standard chromatography columns. The SPEC cartridges used in the present experiments separate $As^{III}$ and $As^{V}$ on the basis of anion exchange.

The first technique described in this chapter is SPEC - Hydride Generation (HG) Atomic Absorption Spectrometry (AAS). Hydride generation (HG) is a chemical derivatization technique that converts some compounds in solution to gaseous hydride. Hydride generation is mainly chosen for sample introduction since it enhances sensitivity and decreases background signal [7]. The selective determination of $As^{III}$ in the presence of $As^{V}$ can be carried out by carefully selecting an acid and optimizing the acid concentration for hydride generation. Sodium borohydride ($NaBH_4$) is used as the reducing agent [8]. The major limitations in using hydride generation for As speciation, however, is that some environmentally and biologically important organoarsenicals such as arsenobetaine do not form an arsine (arsenic hydride) upon treatment with sodium borohydride. Atomic absorption spectrometry is a well established and relatively inexpensive technique that produces low detection limits for As and is easy to use. Disadvantages of this detector include a narrow linear dynamic range, poor sensitivity for refractory forming elements (elements that are resistant to decomposition) and the inability of true multi-element detection.

The second detection method chosen is Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Inductively coupled plasma mass spectrometry is a very powerful detection method. This method is advantageous because of its multi-element capability, wide linear dynamic range, low detection limits and the possibility of on-line isotope dilution [9]. The disadvantages of this detector are that it is expensive, requires skilled operators and has isobaric interferences for some elements (e.g. ArCl interference on As detection). The objective of this chapter is to optimize the separation of $As^{III}$ and $As^{V}$ in pure water and to qualitatively determine these species in well water samples using solid phase extraction cartridges coupled to HG-AAS and ICP-MS.

## 3.1 Experimental Section

### 3.1.0 Reagents

All chemicals were of analytical-reagent grade, unless otherwise noted. Distilled water (Millipore Milli-Q Bedford, MA, USA) was used for the preparation of standards for the SPME-HG-AAS experiments, acid and the mobile phase. For the ICP-MS experiments, HPLC (High performance liquid chromatography) grade water was used. Stock solutions (1000 mg/L As) of $As^{V}$ were prepared from sodium arsenate (Sigma Chemical Co. St. Louis, MO, USA). Solutions of $As^{III}$ (10-20 mg/L) were prepared fresh daily from an arsenic atomic absorption standard solution (Aldrich Chemical Company, Inc., Milwaukee, WI, USA). The stock solutions were stored at 4°C until use. The standards were prepared by the appropriate dilutions of the stock solutions. The standards were usually prepared in the concentration range of 0.1-100 $\mu$g/L. The sodium borohydride ($NaBH_4$) (Aldrich Chemical Company, Inc., powder, 98%) was stabilized by the addition of sodium hydroxide (NaOH) (Fisher Chemicals, Fair Lawn, NJ, USA, solid) to a concentration of 0.1 M NaOH. The phosphate buffer solutions were prepared using sodium dihydrogen orthophosphate (monobasic, 98-102%, BDH Inc., Toronto, ON, Canada) and di-sodium hydrogen orthophosphate (anhydrous, dibasic, 99%, BDH). The phosphate buffer was prepared at 20 mM, 30 mM and 40 mM (Table 3-1).

**Table 3-1: Preparation of Phosphate Mobile Phase**

| | $NaH_2PO_4$* (137.992 g/mol) | $NaHPO_4$* (141.958 g/mol) |
|---|---|---|
| 20 mM | 1.38 g | 1.42 g |
| 30 mM | 2.07 g | 2.13 g |
| 40 mM | 2.76 g | 2.84 g |

*The total volume was 1 L $H_2O$

The second mobile phase tested on the ICP-MS was ammonium bicarbonate (min. 99% ). It was prepared at 20 mM, 30 mM and 40 mM (Table 3-2).

**Table 3-2: Preparation of Ammonium Bicarbonate Mobile Phase**

| | $NH_4HCO_3$ (79.06 g/mol) |
|---|---|
| 20 mM | .7906g |
| 30 mM | 1.1859g |
| 40 mM | 1.5812g |

The pH of the mobile phase and the samples was measured using an accumet® model 15 pH meter. The acid used for hydride generation was hydrochloric acid (HCl) from Fisher Scientific (Nepean, Ontario, Canada) and was appropriately diluted to approximately 10 %. Argon was used as the inert carrier gas.

### 3.1.1 Collection and Pretreatment of Well Water Samples

For the SPEC-ICP-MS analysis, well-water samples from Inner Mongolia were analyzed. Five samples each from three concentration ranges were chosen for the analysis. The concentration ranges were <10$\mu$g/L, 10-100 $\mu$g/L, and >100 $\mu$g/L. The samples were preacidified with $HNO_3$. The acidification would presumably solubilized particulate As and prevent the adsorption of As to the container walls.

### 3.1.2 Analytical Methods

Two methods were used to determine As species. Both methods of As speciation used strong anion exchange cartridges coupled to different detectors. The solid phase extraction cartridges (QMA, Waters/Millipore, Mississauga, ON, CA) were used as the separation column. Each of these disposable cartridges contains approximately 360 mg of silica-based, hydrophilic, polar basic anion exchange phase as the sorbent (pore size 300 A and particle size 37-55 $\mu$m). The cartridge is 2 cm in length and 1.2 cm in diameter and has a void volume of approximately 2.3 mL. Prior to their first use, the cartridges were preconditioned with 15 mL of methanol and then with 15 mL of the eluting buffer. No further conditioning is required as long as the sorbent

does not dry out. Because there were periods of days and sometimes weeks between analyses on the ICP-MS, the cartridges were frequently re-conditioned using methanol and the eluting buffer or exchanged for new ones.

One method of As speciation involved the pairing of the solid phase extraction cartridge (SPEC) coupled to a hydride generation atomic absorption spectrometer system (HG-AAS) (Figure 3-1). The system parameters can be seen in Table 3-3. A 4-channel peristaltic pump with adjustable speed (Gilson, Minipuls 3) was used for this low pressure liquid chromatography system. Accu-Rated Pump Tubes from Mandel Scientific Company Ltd. were used with the peristaltic pump to carry the reagents and sample to the hydride generation system and the detector. Three channels of the peristaltic pump were used to introduce respectively the $NaBH_4$, HCl and mobile phase. A six port sample injection valve (Rheodyne) with a 200 $\mu$l sample loop was used to introduce the sample into the system.

The liquid waste and the gaseous arsenic hydrides are separated in a gas-liquid separator and the waste solutions from the hydride generation constantly drains out via a side arm. The gas liquid separator separates the hydrogen and arsine from the liquid matrix when the reduction reaction is completed. A flow meter is used to regulate argon flow. The injected sample, carried by the phosphate mobile phase (eluent), meets with continuous flows of reagents, HCl and $NaBH_4$. Hydride generation takes place upon the mixing of these solutions and continues in the gas/liquid separator apparatus. The hydrides that are produced are carried to the AAS detector. Flow rates, reagent concentrations and mobile phase pH were optimized, while the other experimental conditions were kept constant. The separation of the peaks, baseline resolution, elution and retention times were the chosen responses to be optimized.

An arsenic UltrAA-lamp (Varian) was operated at 10 mA with an Ultra AA external lamp control module (Varian). Atomization of the arsenic hydrides occurs in a T-shaped quartz

absorption tube. This tube is heated in an electric furnace that is regulated by a temperature controller module (Varian, model ETC-60). Signals from the atomic absorption detector are recorded and processed by a computer with a Varian Star Workstation ADC (analog digital conversion) board and software.

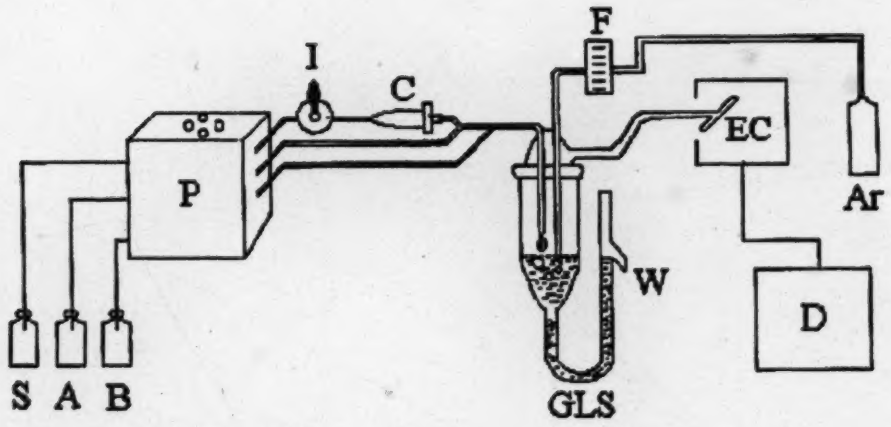


Figure 3-1: A schematic diagram showing chromatographic separation on a solid phase extraction cartridge combined with hydride generation and atomic absorption detection. S, eluting buffer; A, 10% HCl; B, 2% $NaBH_4$; I, sample injection valve; P, peristaltic pump; C, solid phase extraction cartridge; GLS, gas-liquid separator; EC, electrically heated quartz cell; Ar, argon gas; F, flow meter; W, waste; D, atomic absorption detector [10].

The rapid generation of volatile hydrides can be brought about by the addition of an acidified aqueous solution of the sample to a small volume of a 1% aqueous solution of sodium borohydride. $NaBH_4$ is the reducing agent and reduces the $As^{III}$ species to the corresponding hydride by the following overall reaction:

$$3BH_4^- + 3H^+ + 4H_3AsO_3 \rightarrow 3H_3BO_3 + 4AsH_3\uparrow + 3H_2\uparrow$$

In this setup, the sample and acid are mixed first. $As^V$ must be reduced to $As^{III}$ before hydride generation occurs. This mixture then meets up with the $NaBH_4$. The volatile hydride, arsine, is swept into the atomization chamber by an inert gas. The chamber is a quartz t-shaped tube heated to 925°C where decomposition of arsines takes place leading to the formation of free arsenic atoms.

**Table 3-3. Parameter Settings for HG-AAS**

| AAS – Varian Model Spectra AA-5 | |
|---|---|
| **Parameter** | |
| Lamp Current | 10 mA |
| Wavelength | 197.3 nm |
| Spectral Bandwidth | 0.5 nm |
| HCl Flow Rate | Varied |
| HCl Concentration | 10% |
| $NaBH_4$ Flow Rate | Varied |
| $NaBH_4$ Concentration | 1.3% in 0.1M NaOH |
| Carrier Gas | Argon |
| Carrier Gas Flow Rate | 100 mL/min |
| Quartz Cell Temperature | 925°C |

The second method paired the cartridges to a Perkin-Elmer 6100DRC $^{plus}$ inductively coupled plasma-mass spectrometer (Perkin-Elmer/Sciex, USA). The standard liquid sample introduction system consisted of a Meinhard nebulizer coupled to a standard cyclonic spray

chamber (Figure 3-2). For sample transportation, the Series 200 Perkin Elmer pump was connected to the Series 200 autosampler (Perkin Elmer) and to the Meinhard nebulizer.

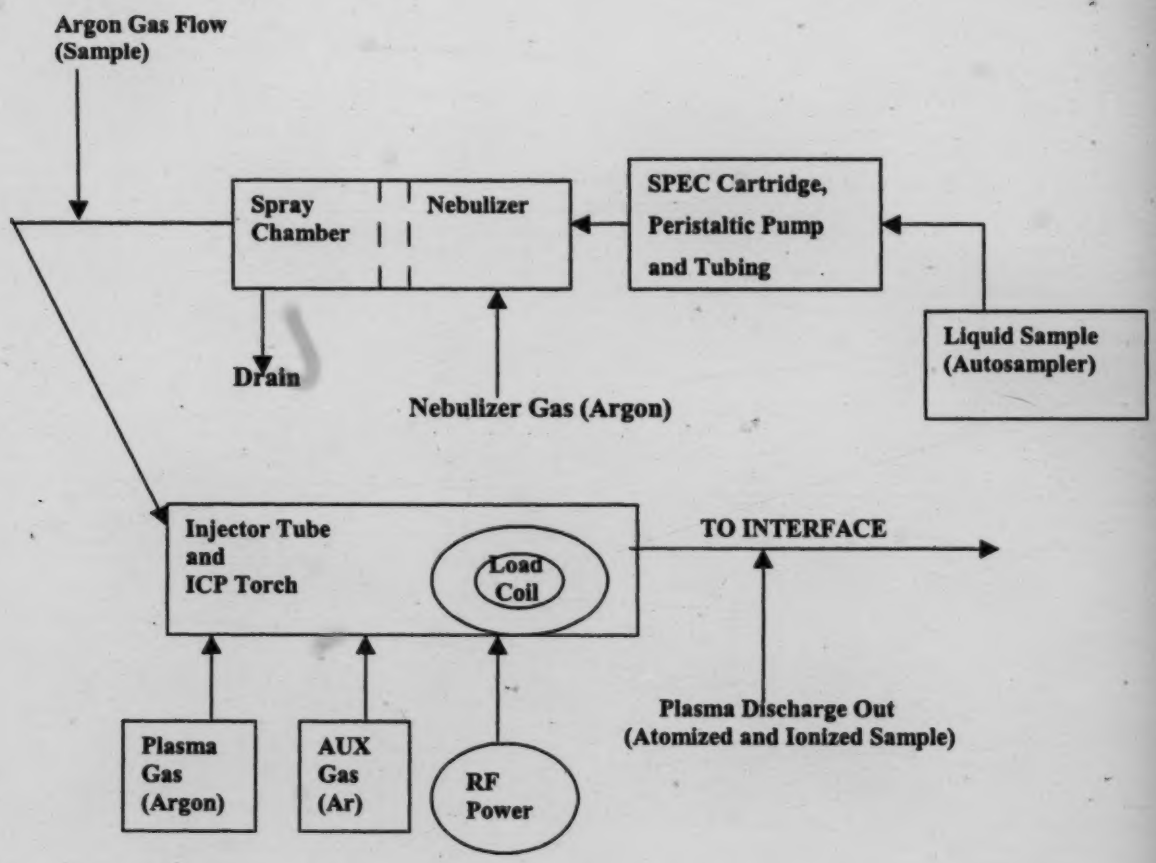


**Figure 3-2:** Sample Introduction system for SPEC-ICP-MS analysis

The parameter settings for the SPEC-ICP-MS experiments can be found in Table 3-4.

**Table 3-4. Parameter Settings for ICP-MS Detection**

| basic parameter | value |
|---|---|
| RF power | 1100 W |
| Ar auxiliary gas flow rate | 1.2 L $min^{-1}$ |
| Ar plasma gas flow rate | 15 L $min^{-1}$ |
| Ar nebulizer gas flow rate | 0.90 L $min^{-1}$ |
| Dwell time per AMU | 100 ms |
| Detector mode | Dual mode |
| Scan mode | Peak hopping |
| Lens | Autolens On |
| Mass (*m/z*) | 75 |
| Sweeps/Reading | 10 |
| Reading/Replicate | 1 |
| Number of Replicates | 3 |

Precision or repeatability was calculated as the coefficient of variation (CV) from peak area measurements of a standard solution containing the As compounds.

## 3.2 Results and Discussion

### 3.2.0 Calibration

Calibration curves for each species were linear for both techniques. For the SPEC-ICP-MS experiments, the results were linear with $R^2$ of 0.99 for both peak area and peak height (Figures 3-3 – 3-6). Future experiments will use an increased number of standard concentrations and a broader range of concentrations to produce a more accurate representation of the calibration. In Figures 3-3 – 3-6, the narrow range and extreme values of some of the calibration standards provide an imprecise $R^2$.

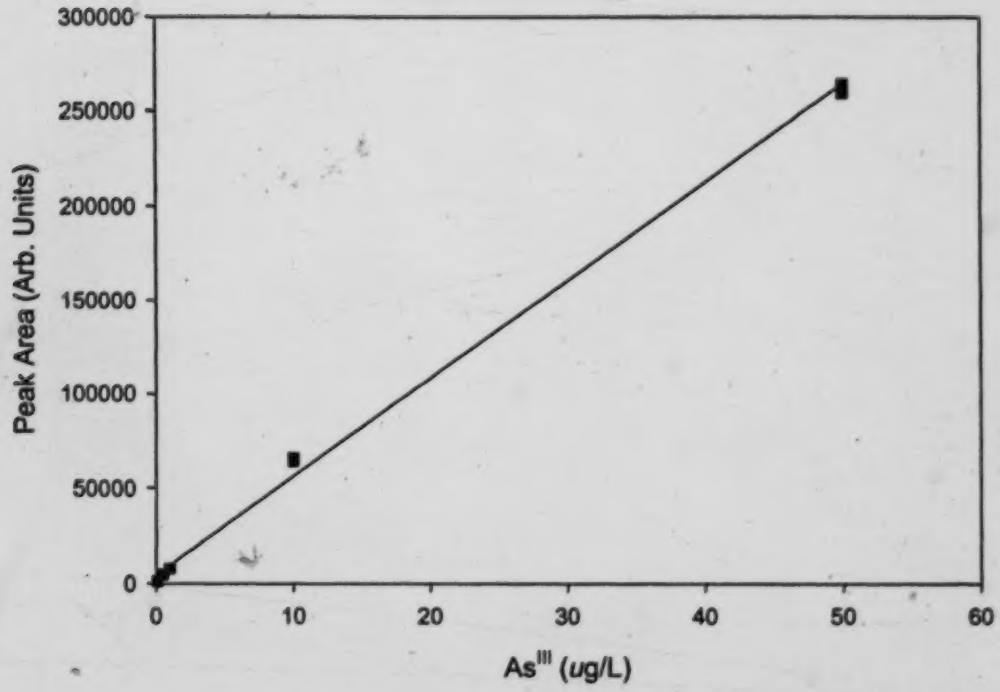


Figure 3-3: Calibration curve for $As^{III}$ using peak area measurements from SPEC-ICP-MS. The SPEC separation buffer was 30mM phosphate at pH 6 and its flow rate was 1.4 mL/min. The sample injection volume was 50 µL. The standard solutions were mixtures of $As^{III}$ and $As^{V}$ at concentrations of 0.1, 0.5, 1, 10 and 50 µg/L of each species. The regression equation was $y=5196.9x + 4243$ with an $R^2 = 0.99$.

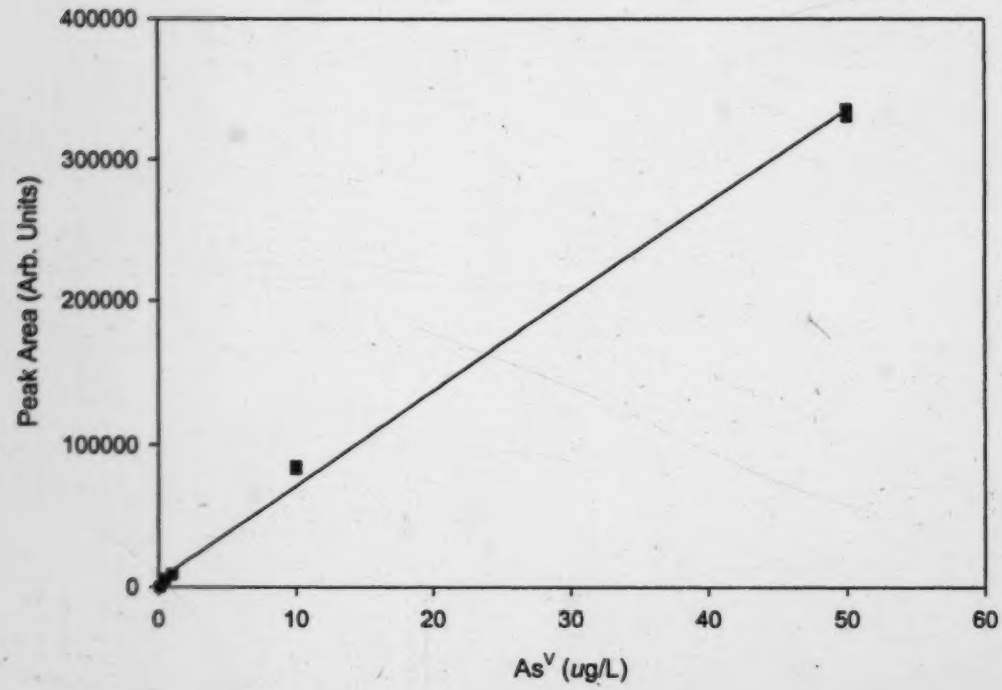


Figure 3-4: Calibration curve for $As^V$ using peak area measurements from SPEC-ICP-MS. The same conditions as Figure 3-3 were used. The regression equation was y=6606.1x + 4998 with an $R^2$ of 0.99.

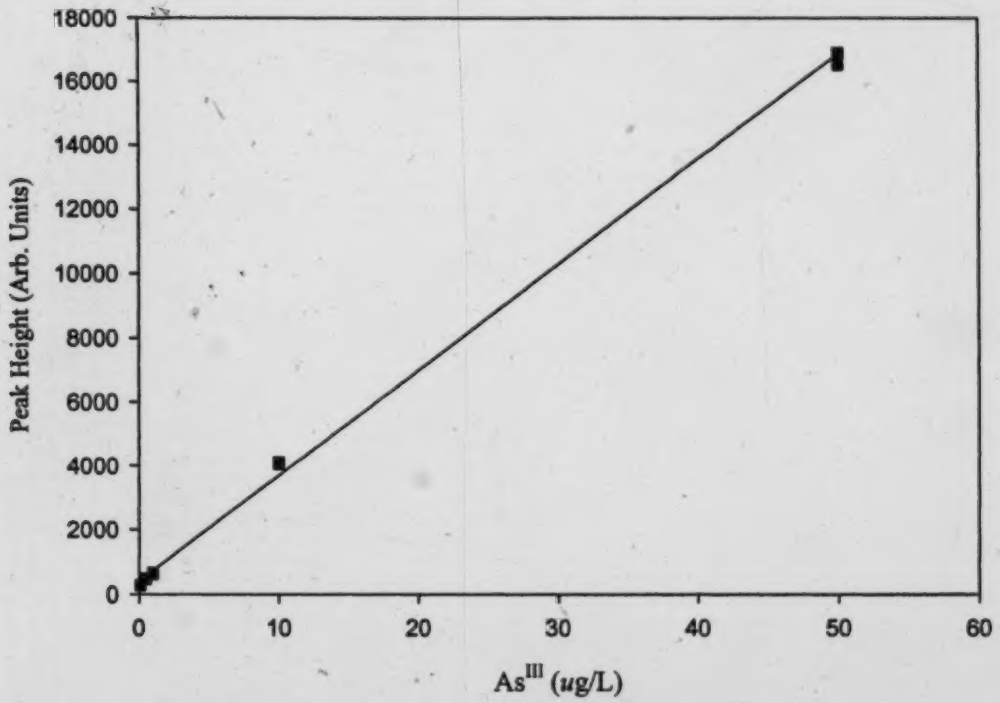


Figure 3-5: Calibration curve for $As^{III}$ using peak height measurements from SPEC-ICP-MS. The same conditions as Figure 3-3 were used. The regression equation was y=328.8x+391 with an $R^2$ of 0.99.

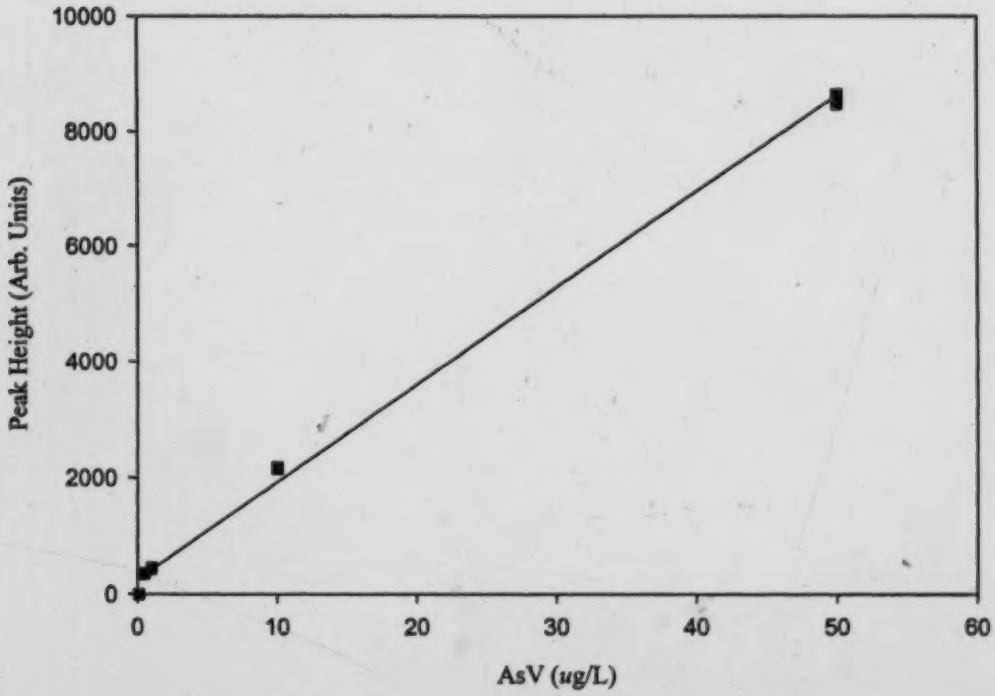


Figure 3-6: Calibration curve for $As^V$ using peak height measurements from SPEC-ICP-MS. The same conditions as Figure 3-3 were used. The regression equation was y=168x+239 with an $R^2$ = 0.99.

The SPEC-HG-AAS analysis resulted in calibration curves with $R^2$ values ranging from 0.98 to 0.99 for peak area and 0.96-0.99 for peak height for both $As^{III}$ and $As^{V}$ (Figure 3-7 – 3-9).

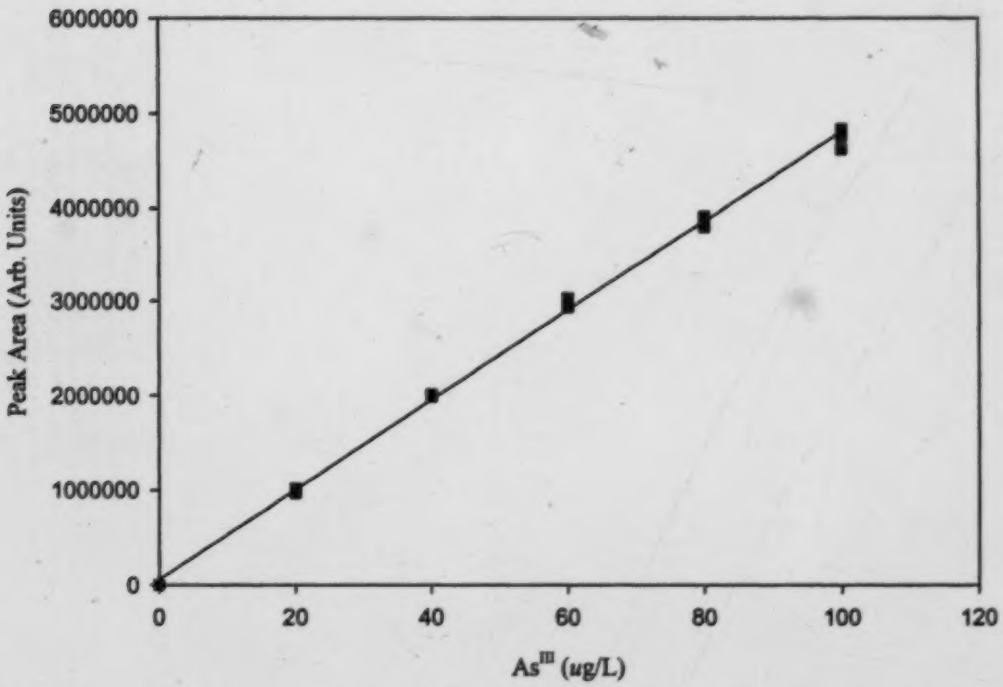


Figure 3-7: Calibration curve for $As^{III}$ using peak area measurements from SPEC-HG-AAS. The SPEC separation buffer was 30 mM phosphate at pH 7 and its flow rate was 4.9 mL/min. For hydride generation, 10% HCl (4.2 mL/min) and 1.3% $NaBH_4$ in 0.1M NaOH (2.6 mL/min) were used. Standards for $As^{III}$ ranged from 0-100 μg/L. Regression equation: y=46747x+108292, $R^2$ = 0.99.

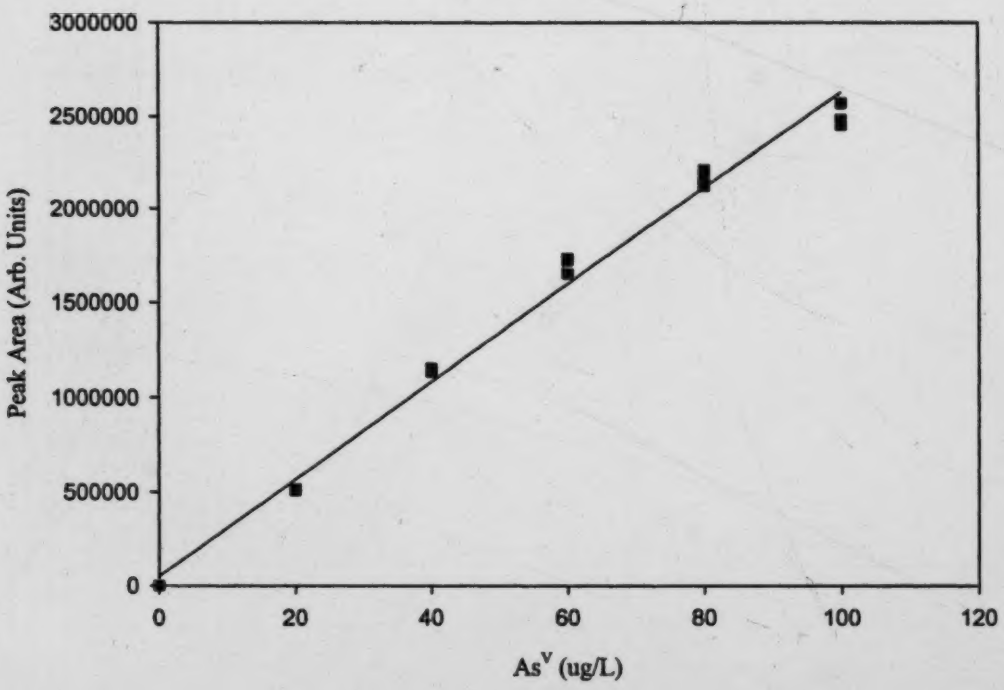


Figure 3-8: Calibration curve for $As^V$ using peak area measurements from SPEC-HG-AAS. The same conditions as Figure 3-7 were used. Regression equation: $y=25780x + 48397$, $R^2 = 0.99$.

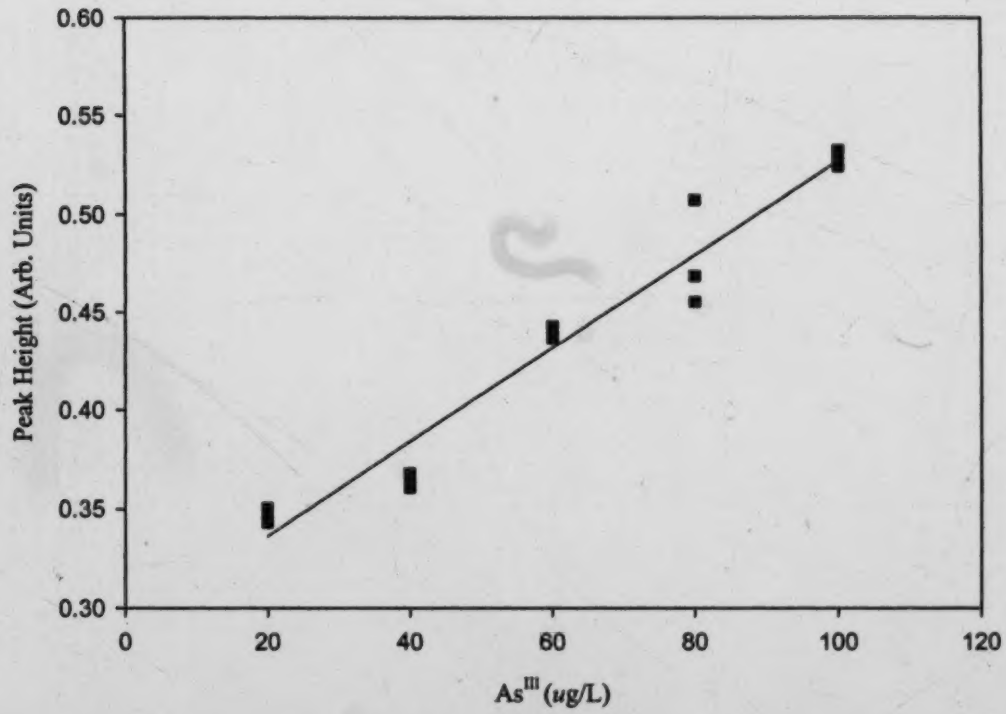


Figure 3-9: Calibration curve for $As^{III}$ using peak height measurements from SPEC-HG-AAS. The SPEC separation buffer was 30mM phosphate buffer at pH 7 and its flow rate was 3.7 mL/min. For hydride generation10% HCl (3.8 mL/min) and 1.3% $NaBH_4$ in 0.1M NaOH (2.1 mL/min) were used. Standards for $As^{III}$ ranged from 0-100 µg/L. The regression equation is $y = 2.39x10^{-3}x + 0.29$ and $R^2 = 0.96$.

### 3.2.1 Separation of $As^{III}$ and $As^{V}$

The inorganic As species, $As^{III}$ and $As^{V}$ were successfully separated using the SPE cartridges. Figures 3-10 and 3-11 show typical chromatograms using the HG-AAS and ICP-MS for detection.

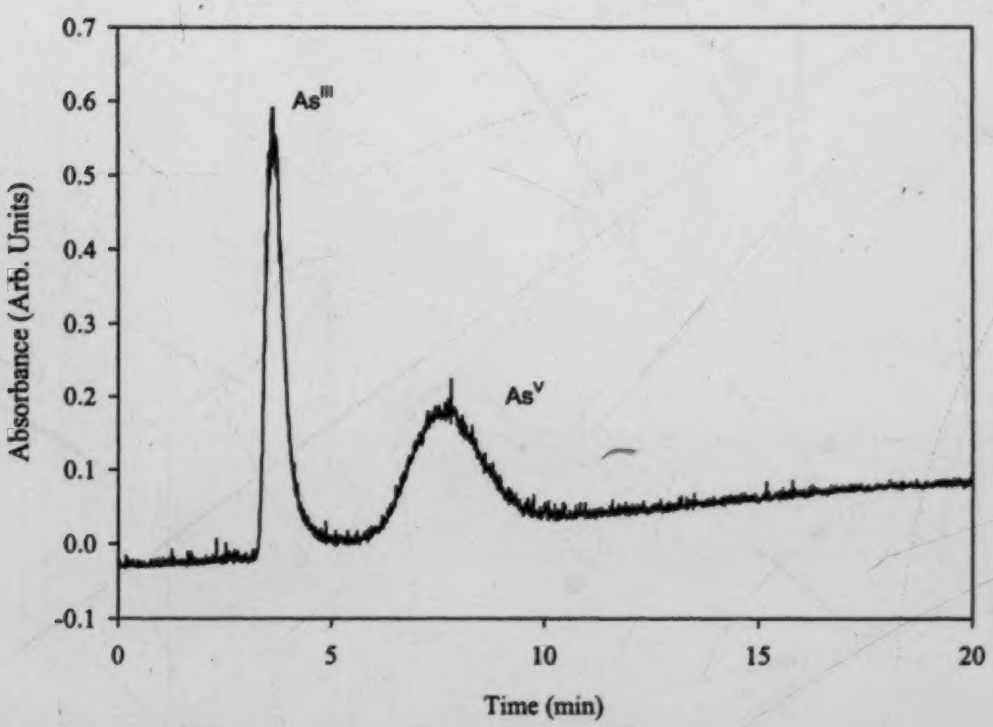


Figure 3-10: A typical chromatogram from SPEC-HG-AAS analysis of $As^{III}$ (100 μg/L) and AsV (60 μg/L). The SPEC separation buffer was 10 mM phosphate at pH 5.7 and its flow rate was 1.6 mL/min. For hydride generation, 10% HCl (4.3 mL/min) and 1.3% $NaBH_4$ (2.2 mL/min) were used.

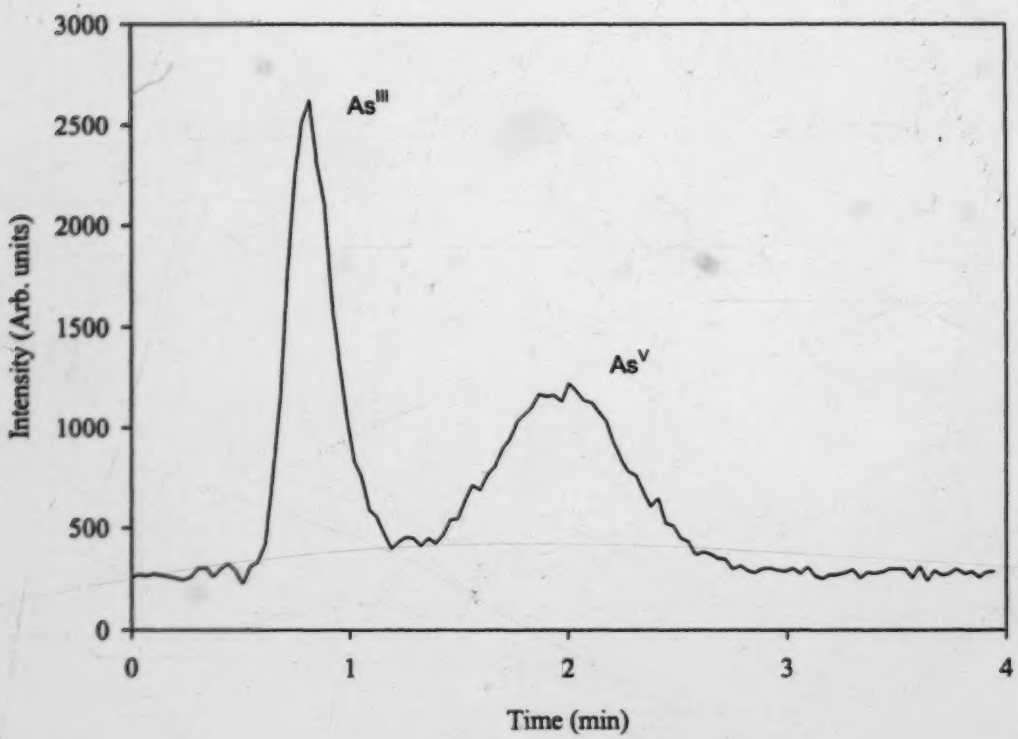


Figure 3-11: A typical chromatogram from SPEC-ICP-MS analysis of $As^{III}$ and $As^{V}$ (10 µg/L each). The SPEC separation buffer was 40mM phosphate at pH 7 and its flow rate was 1.2 mL/min). The sample injection volume was 50µL.

### 3.2.2 Precision

The precision of the techniques was determined by the injection of standard solutions. For the SPEC-HG-AAS analysis, multiple injections of 100 μg/L $As^{III}$ alone (CV = 2.8%) (Figure 3-12) and triplicate injections of $As^{III}$ at concentrations of 20 μg/L, 40 μg/L and 60 μg/L (Figure 3-13) showed that peak area was reproducible with a precision typically ranging from 1-6%. However, the increase in absorbance (peak height) was not linear with higher concentrations of As. The reasons for this nonlinearity are unknown.

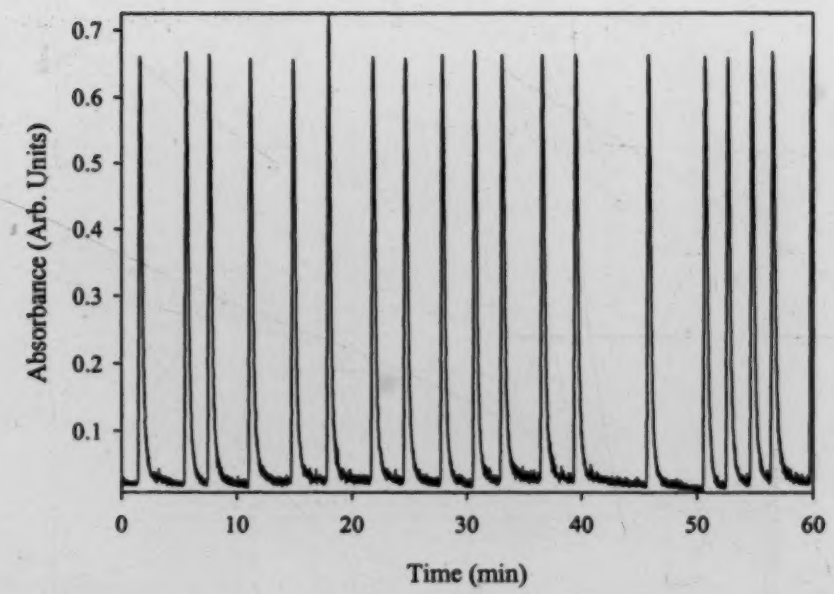


Figure 3-12: Repeat measurements of 100 μg/L $As^{III}$ using SPEC-HG-AAS. The same conditions as shown in Figure 3-7 were used.

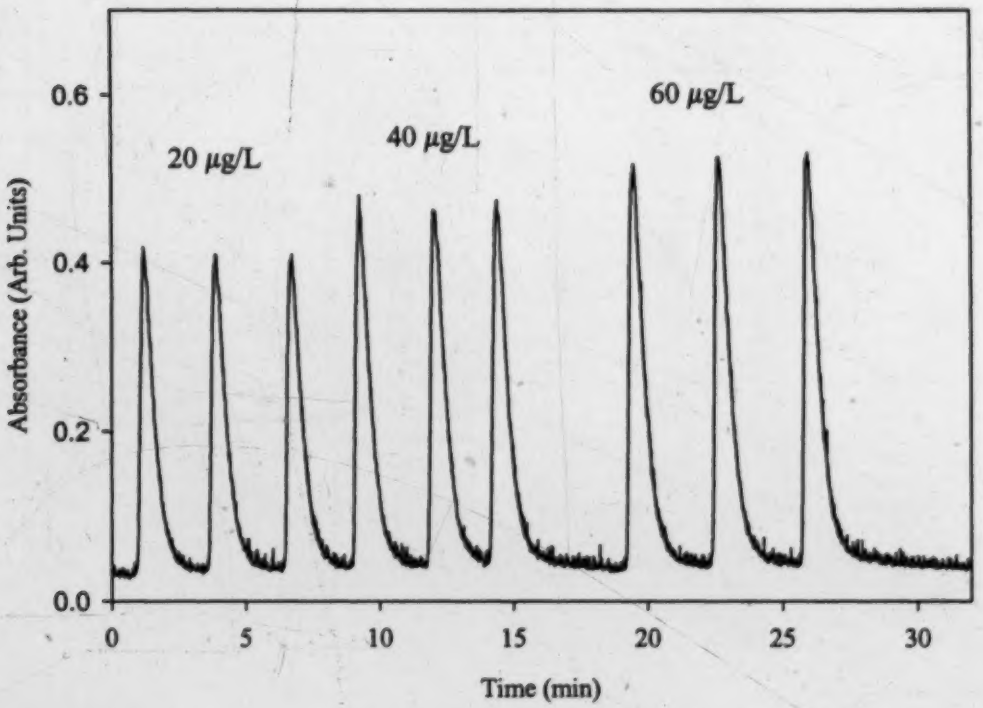


Figure 3-13: Triplicate analyses of $As^{III}$ at concentrations of 20 µg/L, 40 µg/L and 60 µg/L using SPEC-HG-AAS. The same conditions as shown in Figure 3-7 were used.

For the ICP-MS results, triplicate injections of a mixture containing $As^{III}$ and $As^{V}$ at 25μg/L each gave peak areas with a coefficient of variation of no higher than 6% (Figure 3-14). Three chromatograms from the triplicate analysis are superimposed.

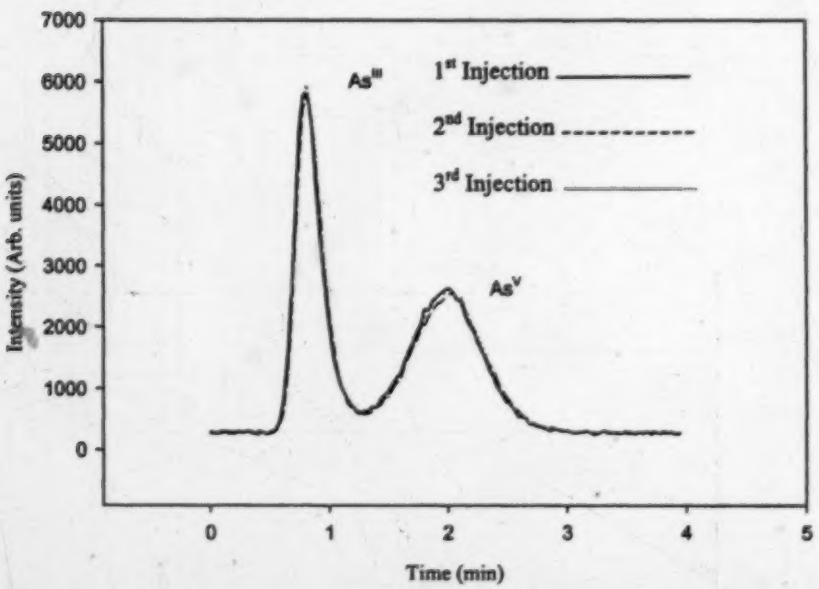


Figure 3-14 : Triplicate measurement of $As^{III}$ and $As^{V}$ (25 μg/L each) using SPEC-ICP-MS. The SPEC separation buffer was 40mM phosphate at pH 7 and its flow rate was 1.2mL/min. The sample injection volume was 50μL.

### 3.2.3 Optimization

Studies were carried out to optimize the separation conditions. For the SPEC-HG-AAS experiments, the following parameters were optimized: the HCl flow rate, $NaBH_4$ concentration, the pH and concentration of the mobile phase. In the SPEC-ICP-MS experiments, the mobile phase concentration, pH and flow rates were optimized.

#### 3.2.3.0 HCl Concentration

Arsine generation is acid dependent and the acid choice and concentration will affect the efficiency of the arsine generation [11,12]. Studies have shown that for $As^{III}$ and $As^{V}$, the signal rapidly increases when the HCl concentration is increased up to 0.4 M and then the signals gradually increase with increasing HCl concentrations and reach maximum and constant values at concentrations from 0.6 – 6M [11]. The concentration of the acid used for arsine generation also produces different response profiles depending on the medium in which As species are prepared [11].

#### 3.2.3.1 HCl Flow Rate for Hydride Generation

The efficiency of the arsine generation can be affected by the HCl flow rate at a constant HCl concentration. The HCl flow rate was varied from 0.61-2.02 mL/min. The retention times of $As^{III}$ and $As^{V}$ were not affected by variation in the HCl flow rate. However, the peak height and peak area were affected by HCl flow (Figure 3-15 and 3-16). The peak area and peak height increase rapidly with increasing HCl pump speed and then appear to plateau. Therefore, there appears to be a minimum flow rate necessary to obtain consistent results. The optimum flow rate chosen for HCl will depend on many factors, including: HCl concentration, mobile phase concentration, mobile phase pH, $NaBH_4$ flow rate and $NaBH_4$ concentration. The flow rate is limited by the tubing used in the experiment and the low pressure peristaltic pumps. At a certain

point one should consider changing the HCl concentration instead of increasing the flow rate as the peristaltic pumps used cannot handle the high pressure.

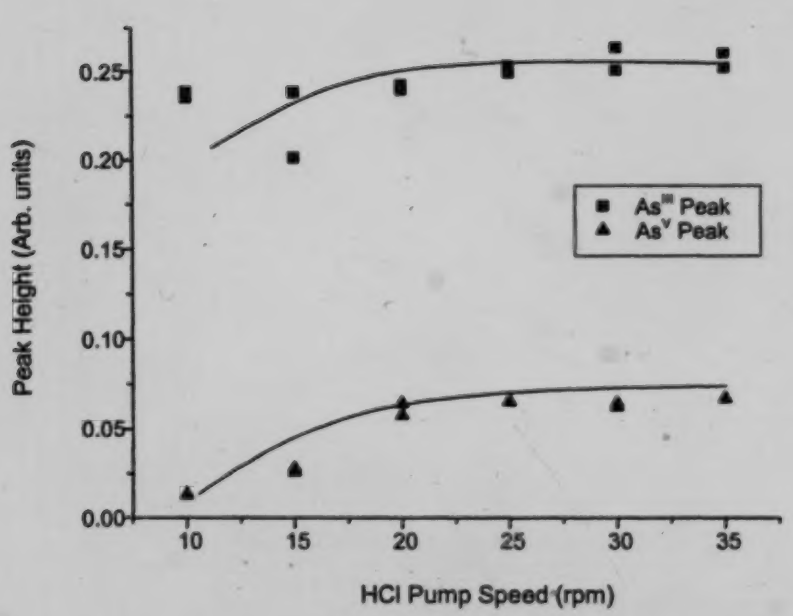


Figure 3-15: Effect of HCl pump speed on peak height of $As^{III}$ (100 μg/L) and $As^{V}$ (60 μg/L) $As^{V}$ using SPEC-HG-AAS. The SPEC separation buffer was 20mM phosphate at pH 7 and its flow rate was 1.4 mL/min. For hydride generation 10% HCl and 2%$NaBH_4$ (1.7 mL/min) were used.

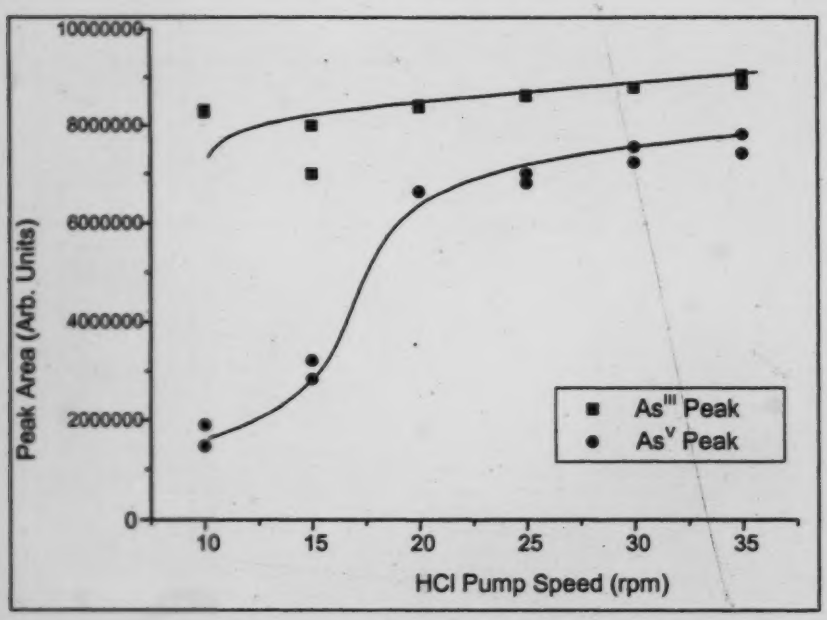


Figure 3-16 : Effect of HCl pump speed on peak area of $As^{III}$ (100 µg/L) and $As^{V}$ (60 µg/L) using SPEC-HG-AAS. The same conditions as shown in Figure 3-15 were used.

### 3.2.3.2 $NaBH_4$ Concentration

The sensitivities of the hydride forming analytes are dependent on the concentration of $NaBH_4$. There is an optimum range of $NaBH_4$ depending on the analyte. In previous experiments it was found that when using atomic fluorescence, the signal to noise ratio was improved when a lower concentration of $NaBH_4$ was used. For a 2% solution in 0.1M NaOH, the signal to noise ratio for $As^{III}$ ( 5 $\mu$g/L) and $As^{V}$ (5 $\mu$g/L) was 8.6 and 3.9 respectively. For a 1% solution in 0.1M NaOH, the signal to noise ratio for $As^{III}$ (5 $\mu$g/L) and $As^{V}$ (5 $\mu$g/L) was 23 and 7.5 respectively. Detection limits may therefore be reduced by varying the $NaBH_4$ concentrations. The reason for the decreased signal at higher concentrations of $NaBH_4$ may be due to the increased hydrogen concentration introduced into the reaction cell (HG-AAS) or the plasma (ICP-MS) [12,13]. The excess hydrogen produces a dilution effect. The $NaBH_4$ concentration varied from 1-1.3% in the present SPEC-HG-AAS experiments.

### 3.2.3.3 Argon Flow Rate

For the SPEC-HG-AAS experiments, the argon flow rate was varied from 80 – 240 mL/min. The retention times and baseline resolution were not significantly affected by the argon flow rate. The optimal flow rate chosen will in part depend on the volume and design of the gas liquid separator. For the present experimental set-up, the optimum argon flow rate was 100 – 120 mL/min. A higher flow rate resulted in reduced peak height and peak areas. Higher argon flow rates may produce a dilution effect and lower sensitivity [14]. Lower flow rates may decrease the detection limits and improve accuracy.

### 3.2.3.4 Mobile Phase Flow Rate

In the SPEC-HG-AAS analysis, the eluent (phosphate buffer) flow rate was varied from 0.87 mL/min to 3.74 mL/min. In the SPEC-ICP-MS experiments, the flow rate was varied from 0.5-1.4 mL/min. The flow rate chosen for both detectors is limited by the tubing and low

pressure peristaltic pumps. The flow rate in the ICP-MS experiments is not only limited by this low pressure system (cartridge and peristaltic pump), but also by the efficiency of the nebulizer. Higher flow rates will decrease the nebulization efficiency. For both techniques, the retention time (measured at peak maximum) of each As species decreases as the flow rate is increased (Figure 3-17). The separation, or resolution of the two peaks may be compromised by varying the flow rate. Figure 3-18 gives an example of the effects of varying flow rates on the separation of $As^{III}$ and $As^{V}$.

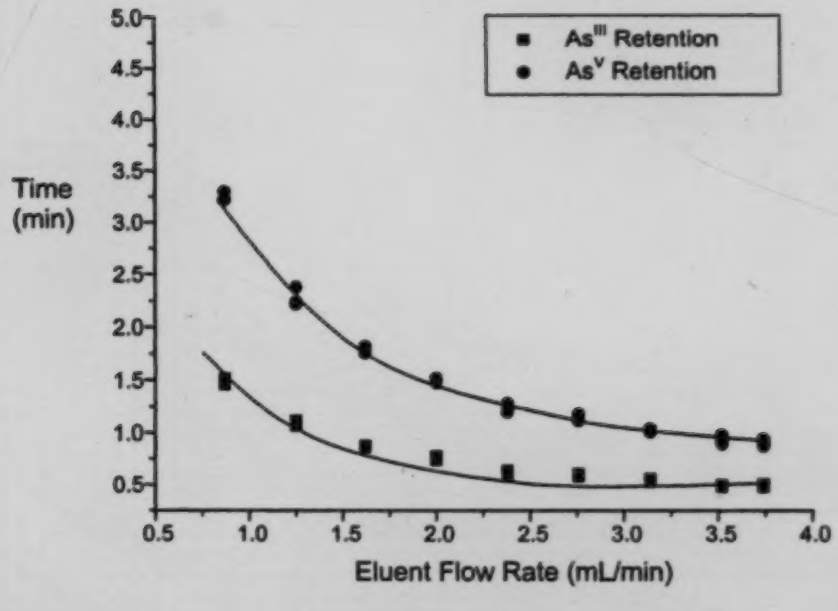


Figure 3-17: Effect of eluent flow rate on retention time of $As^{III}$ (100 µg/L) and $As^{V}$ (60µg/L) using SPEC-HG-AAS. The SPEC separation buffer was 40 mM phosphate at pH 7. For hydride generation, 10% HCl (3.5 mL/min) and 2% $NaBH_4$ (2.2 mL/min) were used.

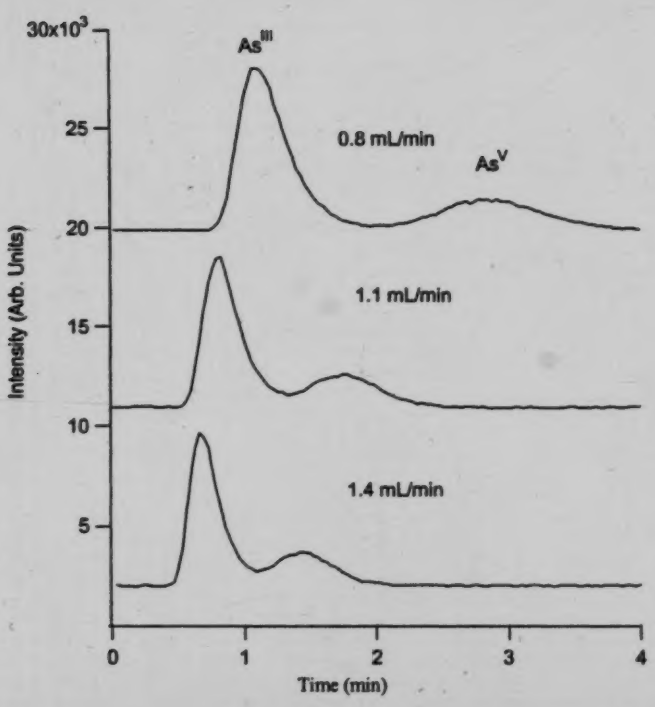


Figure 3-18: Effect of eluent flow rate on retention times and separation of $As^{III}$ (50 µg/L) and $As^{V}$ (25 µg/L) using SPEC-ICP-MS. The SPEC separation buffer was 40mM phosphate at pH 6. The sample injection volume was 50 µL.

It is important to prevent overlap of the peaks which may occur at high flow rates. A flow rate that can efficiently separate low and high concentrations must be determined. For the ICP-MS experiments, there did not appear to be overlap of the peaks at high As concentrations in standards and well water samples (Figure 3-19 and 3-20). The results indicate that the matrix of the well water sample is not affecting the separation of $As^{III}$ and $As^{V}$.

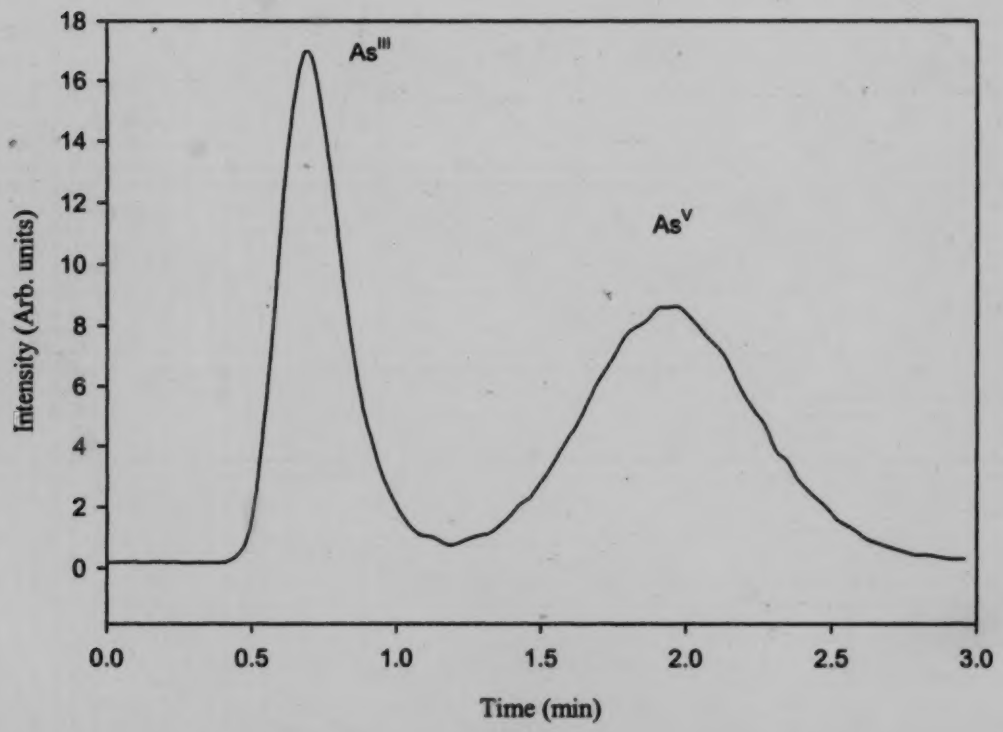


Figure 3-19: SPEC-ICP-MS analysis of $As^{III}$ and $As^{V}$ (50µg/L each) in standard solution. 30mM phosphate buffer at pH 6 was used as the eluent and its flow rate was at a maximum of 1.4mL/min. The sample injection volume was 50µL.

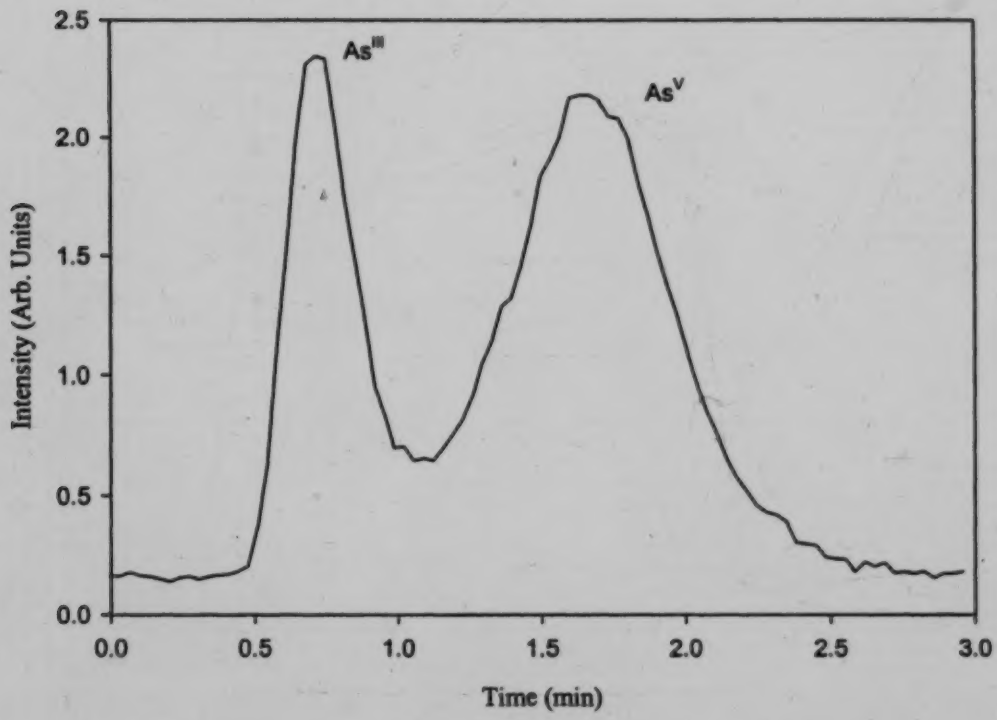


Figure 3-20: Analysis of As species (48.7 µg/L total As) in a well water sample by SPEC-ICP-MS. The same conditions as shown in Figure 3-19 were used.

### 3.2.3.5 Mobile Phase Concentration

The concentration of the phosphate buffer does not significantly affect the retention of $As^{III}$ (Figure 3-21). However, the retention time of $As^{V}$ is affected by the concentration of phosphate (Figure 3-21). As the phosphate concentration is decreased, the retention time of $As^{V}$ is increased. The $As^{III}$ and $As^{V}$ peak separation can be increased by using a less concentrated mobile phase [13]. However, if the concentration of the buffer is too low, the retention time of $As^{V}$ may be so high that the technique is time-consuming. For the SPEC-HG-AAS experiments, though it appeared that 10mM was the optimum mobile phase concentration for complete separation of the two species, the $As^{V}$ peak took a very long time to elute. Figure 3-22 shows that with a phosphate buffer concentration of 10mM, the $As^{V}$ takes approximately 5 minutes to elute (Figure 3-22). The $As^{V}$ peak is very broad making quantification difficult. The optimal concentration for the phosphate buffer for both techniques was determined to be 30 mM. At this concentration, there was near baseline resolution and the total elution time (time for each As species to completely leave the column) was less than 5 minutes.

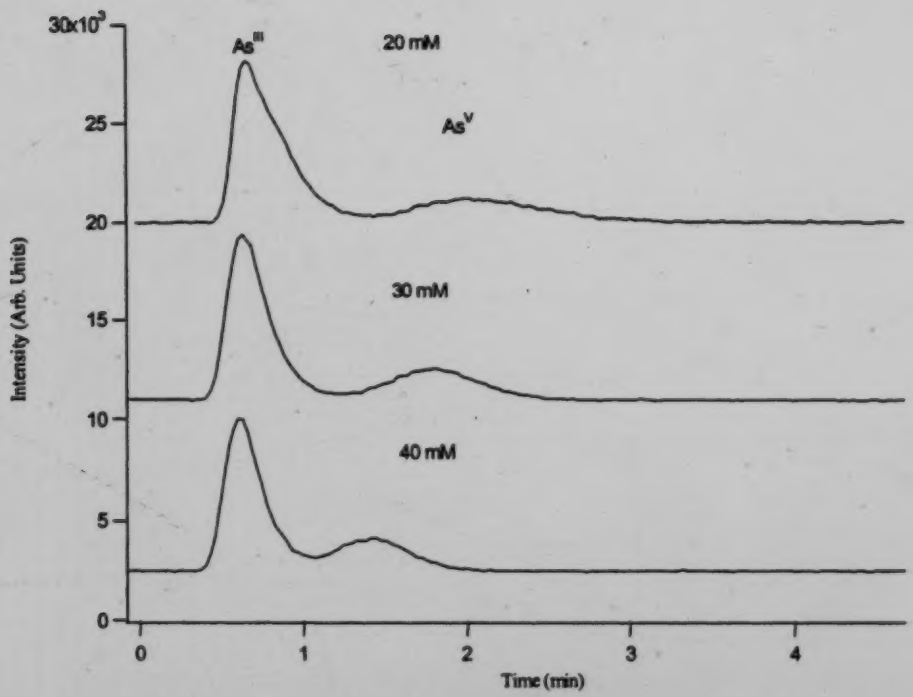


Figure 3-21: The effect of phosphate concentration on the separation of $As^{III}$ (50 μg/L) and $As^{V}$ (25 μg/L) using SPEC-ICP-MS. The SPEC phosphate buffer was prepared at pH 6 and its flow rate was 1.1mL/min. The sample injection volume was 50 μL.

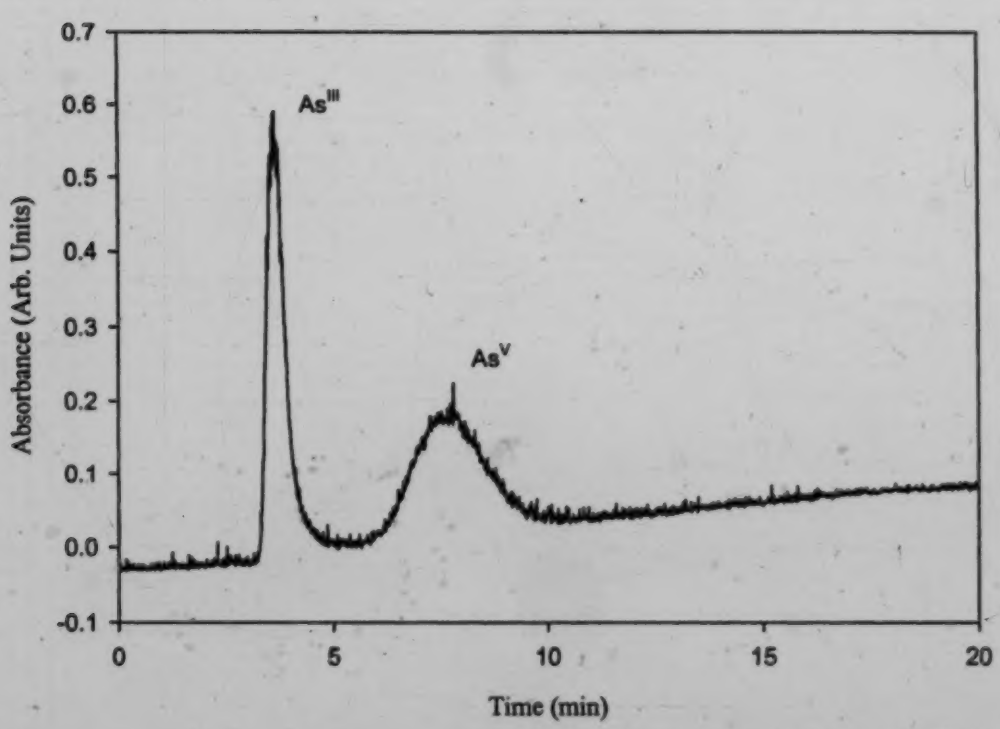


Figure 3-22: A chromatogram showing the separation of $As^{III}$ (100 µg/L) and $As^{V}$ (60 µg/L) by SPEC-HG-AAS. The SPEC separation buffer was10mM phosphate at pH 5.7 as the eluent with a flow rate of 1.5 mL/min. For hydride generation 10% HCl (4.2 mL/min) and 1.3% $NaBH_4$ in 0.1M NaOH (2.6 mL/min) were used.

### 3.2.2.6 Mobile Phase pH

The mobile phase pH was varied from 5-7. The pH range is limited by the choice of chromatographic column. The optimal pH is between 2 and 8 for the SPEC cartridges. If the pH is too acidic, siloxane bonds may hydrolyze. If the pH is higher than 8, the silica in the cartridge becomes unstable. The retention time for $As^{III}$ does not change with pH variation. The retention time of $As^{V}$ increases with increase of pH from 5-7 (Figure 3.23). In these experiments, an anion exchange column is used. The relationship observed is expected because as the pH increases, the $As^{V}$ becomes more ionized and in turn is retained longer by the column. The composition of the mobile phase in addition to the mobile phase pH will affect the retention the analyte.

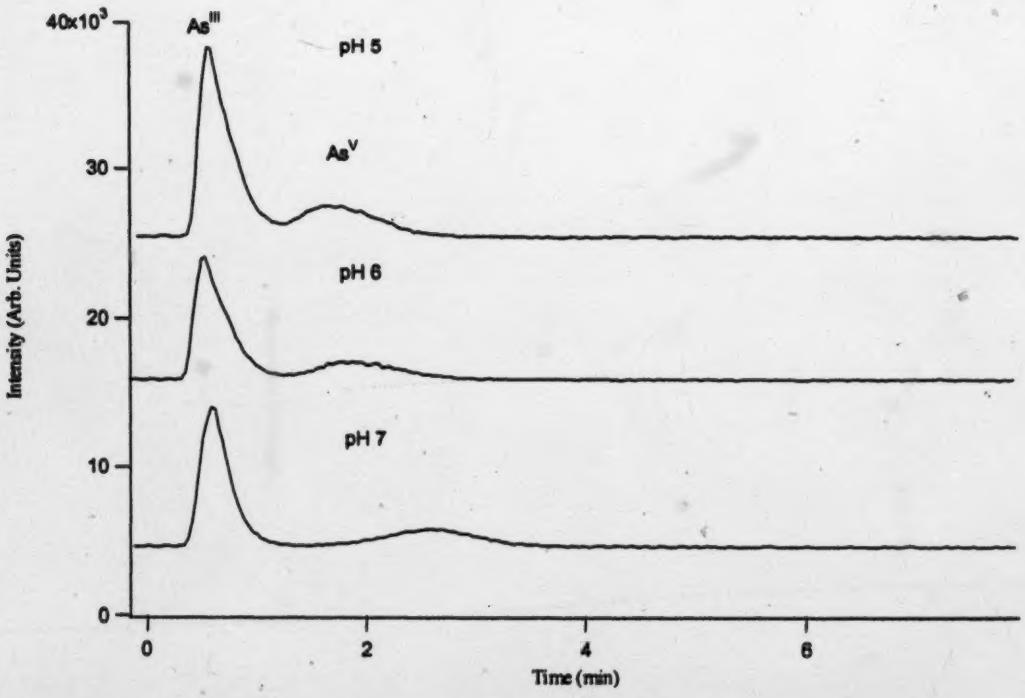


Figure 3-23: The effect of eluent pH on the separation of $As^{III}$ (50 μg/L) and $As^{V}$ (25 μg/L) using SPEC-ICP-MS. The SPEC separation buffer was 20 mM phosphate and its flow rate was 1.4 mL/min. The sample injection volume was 50 μL.

### 3.2.3.7 Choice of Mobile Phase

Although phosphate is a very useful mobile phase for the separation of $As^{III}$ and $As^{V}$ as we have shown, some phosphate reagents contain high background As (up to 0.5 μg/L). High concentrations of Na-phosphate can also cause blockage of the nebulizer and the sampling and skimmer cones when used for long periods [15]. This buildup of salts leads to instrumental drift [15]. In the SPEC-ICP-MS experiments, a loss of sensitivity was observed within a few hours of analysis. Heitkemper et al. reported that concentrations of 50 mM phosphate buffers caused the rapid erosion and clogging of the nickel sampling cone [16]. Hydride generation eliminates this problem because the As is converted to its gaseous hydride which is separated without the associated dissolved solids.

In an attempt to search for an alternative mobile phase, we examined the use of ammonium bicarbonate. Ammonium bicarbonate was used because it was not expected to cause any severe interference problems such as physical clogging of the sampler or skimmer cones of the ICP-MS [17]. However, we found that the separation using this buffer was highly variable. The retention of $As^{V}$ was also unreasonably long and the peak broadening was significant. At 20 mM ammonium bicarbonate (pH 7), $As^{V}$ was not eluting after 8 minutes. At pH 3.3, $As^{V}$ took 5 minutes to elute. The optimal pH of the ammonium bicarbonate solution for its buffer capacity is approximately 10.3 (pKa value). However, this pH could not be used with the silica column. Therefore, we decided to use phosphate buffer for the remainder of the study.

## 3.3 Well Water Samples

Well water samples from Inner Mongolia were analyzed using the SPEC-ICP-MS technique. Examples from the analysis of well water samples containing low (<10 μg/L) (Figure

3.24), medium (10-100 μg/L)(Figure 3.25) and high (>100 μg/L)(Figure 3.26) concentrations of As are shown.

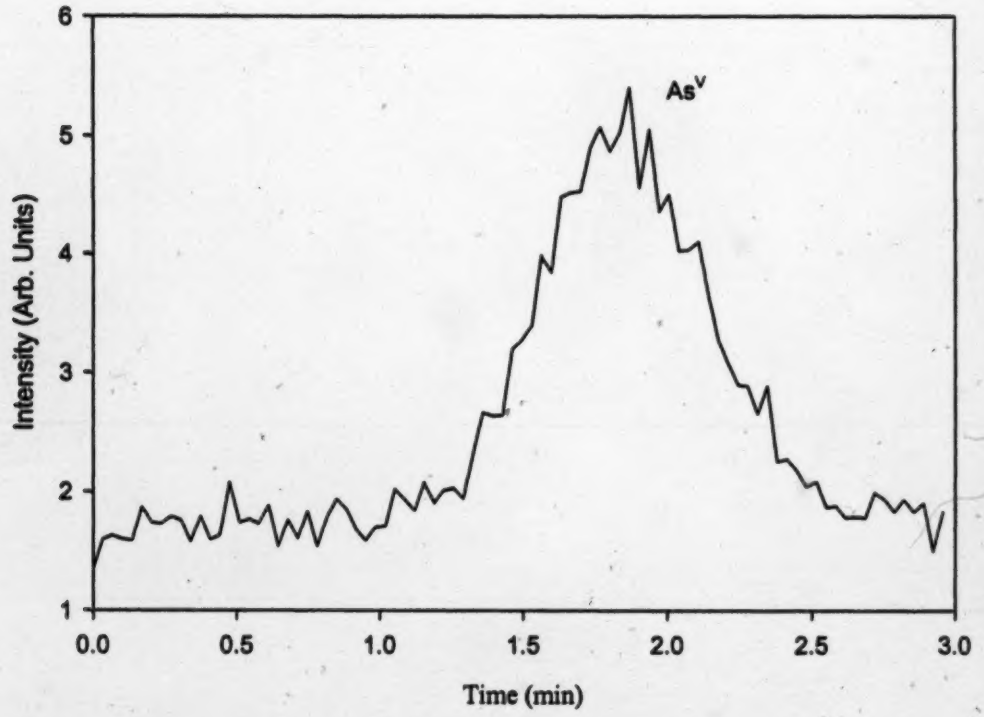


Figure 3.24: SPEC-ICP-MS analysis of a well water sample from Inner Mongolia. As$^{V}$ was the main As species and its concentration was 5 μg/L. SPEC separation buffer was 30 mM phosphate at pH 7.0 and its flow rate was 1.2 mL/min. A 50 μL water sample was injected for analysis.

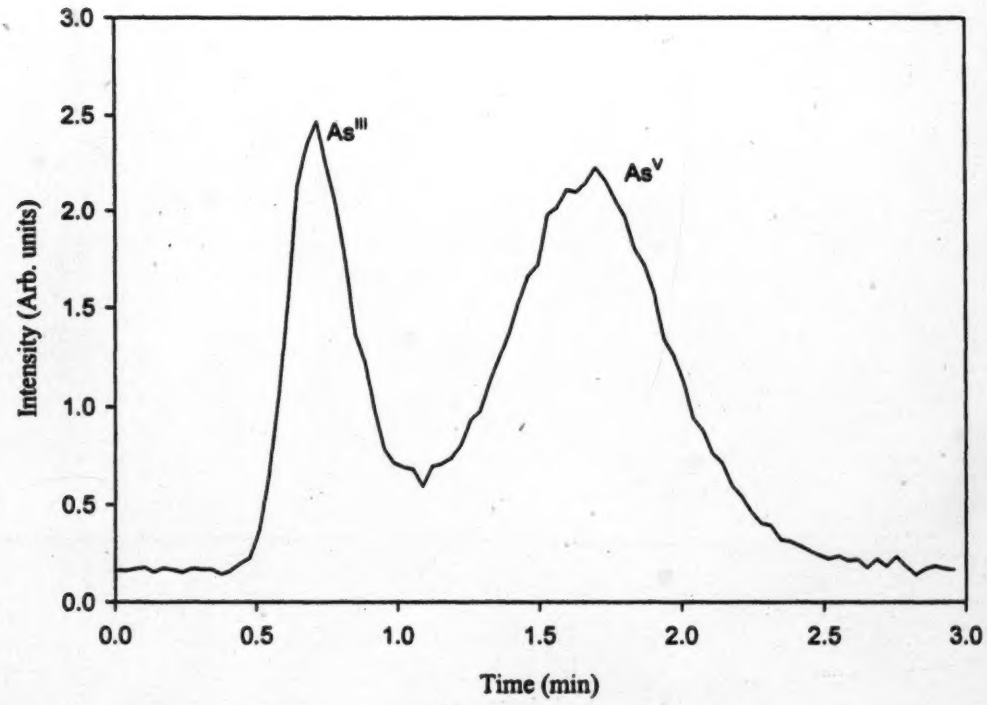


Figure 3-25: SPEC-ICP-MS analysis of a well water sample from Inner Mongolia. $As^{V}$ and $As^{III}$ were detected (Total As 48 $\mu$g/L). The same conditions as shown in Figure 3-24 were used.

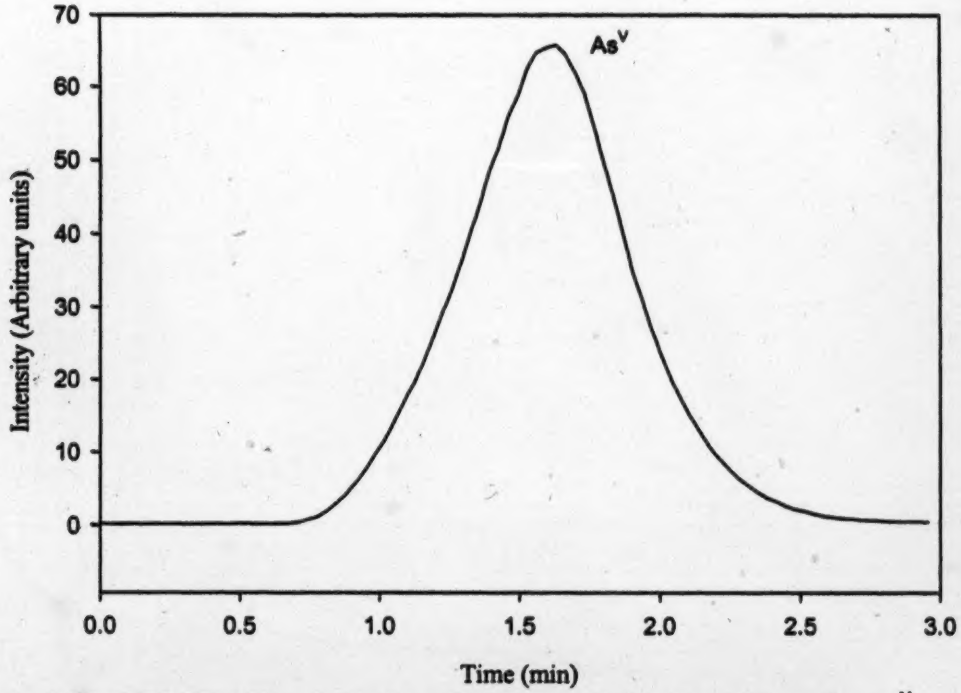


Figure 3-26: SPEC-ICP-MS analysis of a well water sample from Inner Mongolia. $As^V$ was the main As species and its concentration was 920 μg/L. The same conditions as shown in Figure 3-24 were used.

To examine whether sample acidity and matrix affect the separation efficiency, analysis of a standard solution (deionized water) and well water are compared. The retention time of $As^{III}$ was not significantly affected by the sample matrix (Figure 3-27). The retention time of $As^{V}$ differed between the two matrices. This is probably because a high ionic strength or a different acidity of the well water may affect the ion-exchange process. The pH of the well water sample was between 1.4 and 1.6 whereas the pH of the standard was near neutral. The retention time for $As^{V}$ reduces with a lower pH as shown earlier in Figure 3-23. The results in Figure 3-23 and Figure 3-27 are consistent.

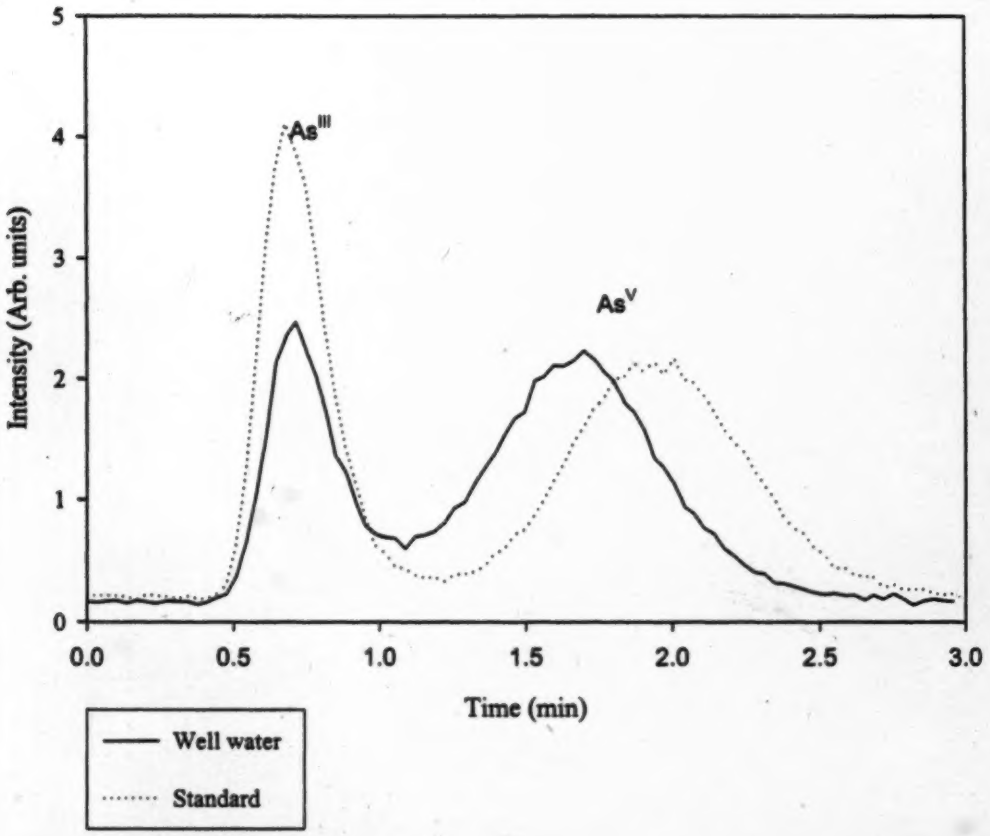


Figure 3.27: Comparison of retention times of $As^{III}$ and $As^{V}$ in a well water sample (Total As 48 $\mu$g/L) and a standard solution (10 $\mu$g/L each) using SPEC-ICPMS. The same conditions as shown in Figure 3-24 were used.

Although the acidified water samples result in a shorter retention time for $As^{V}$, the separation and determination of $As^{III}$ and $As^{V}$ species are not significantly affected. Triplicate analyses of a well water sample show that the speciation of $As^{III}$ and $As^{V}$ was reproducible (Figure 3-28).

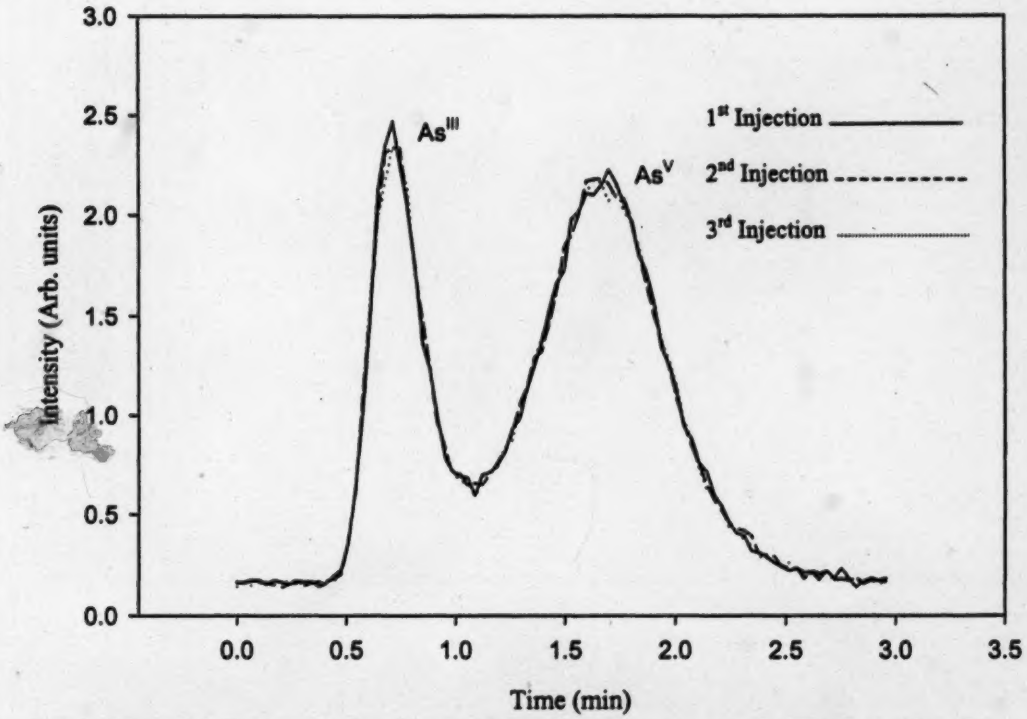


Figure 3-28: Triplicate analysis of Inner Mongolia well water sample (Total As 48 $\mu g/L$) using SPEC-ICP-MS. The same conditions as those shown in Figure 3-24 were used. Three chromatograms from the triplicate analysis are superimposed.

### 3.4 Conclusions

This study focused on the separation of $As^{III}$ and $As^{V}$ in water using SPE cartridges. The SPE cartridges separate $As^{III}$ and $As^{V}$ in well water in under 5 minutes. The rapid and efficient determination of As species in well water will enable the development of suitable treatment and removal methods. If the predominant species present in well water is $As^{V}$, then the As can be easily be removed using an adsorbent such as an Fe oxide material. However, if a significant percentage of the total As is present as $As^{III}$, then some form of pretreatment will be necessary. The determination of total As will not provide sufficient information. Both HG-AAS and ICP-MS can be used for detection of As in water. The technique is suitable for a high volume of samples and is additionally appealing due to the low cost of the cartridges.

The samples in this study had been preacidified to approximately pH 1.4-1.6. Studies should compare the results of As determination in acidified and non-acidified samples to examine the dependence of the retention time and peak area on the pH of a water sample. Mattusch and Weinrich determined that the subsequent acidification of an effluent sample from pH 6.5 to 2 by HCl led to a shift in the peak maximum, to shorter retention times and to an enhanced $As^{V}$ signal[18]. It would be beneficial to determine if the reproducibility is similar to the results from samples that were acidified.

Quantitative studies will be carried out. It is recommended that the blanks, matrix-matched standards and standard reference materials be run throughout the experiments to ensure the accuracy of the experiments. By calibrating often, the sensitivity changes in the instruments will be able to be monitored more closely.

## 3.5 References:


[1] W.R. Cullen, K.J. Reimer, Chem. Rev. 89 (1989) 713.

[2] A.H. Welch, Ground water 38 (2000) 589.

[3] M. Edwards, S. Patel, L. McNeill, H.W. Chen, M.M. Frey, A.D. Eaton, R.C. Antweiler, H.E. Taylor, J. Am. Water Works. Assoc. 90 (1998) 103.

[4] H.W. Chen, M.M. Frey, D. Clifford, L.S. McNeill, M. Edwards, J. Am. Water Works. Assoc. 91 (1999) 74.

[5] Z. Gong, X. Lu, M. Ma, C. Watt, X.C. Le, Talanta 58 (2002) 77.

[6] S. Saverwyns, X. Zhang, F. Vanhaecke, R. Cornelis, L. Moens, R. Dams, J. Anal. At. Spectrom. 12 (1997) 1047.

[7] S.D. Richardson, Anal. Chem. 73 (2001) 2719.

[8] A.G. Howard, J. Anal. At. Spectrom. 12 (1997) 267.

[9] J. Szpunar, Analyst 120 (2000) 963.

[10] S. Yalcin, X.C. Le, Talanta 47 (1998) 787.

[11] P. Carrero, A. Malave, J.L. Burguera, M. Burguera, C. Rondon, Anal. Chim. Acta 438 (2001) 195.

[12] B. Klaue, J.D. Blum, Anal. Chem. 71 (1999) 1408.

[13] B.A. Manning, D.A. Martens, Environ. Sci. Technol. 31 (1997) 171.

[14] R. Torralba, M. Bonilla, A. Palacios, C. Camara, Analusis 22 (1994) 478.

[15] M. Burguera, J.L. Burguera, Roum. Chem. Quart. Rev. 5 (1997) 183.

[16] D.T. Heitkemper, J.T. Creed, J. Caruso, F.L. Fricke, J. Anal. At. Spectrom. 4 (1989) 279.

[17] E.H. Larsen, Spectrochim. Acta B53 (1998) 253.

[18] J. Mattusch, R. Wennrich, Anal. Chem. 70 (1998) 3649.

## Chapter 4. Determination of Particulate Arsenic in Well Water

### 4.0 Introduction

Arsenic is present in a variety of inorganic and organic chemical forms in water. In ground water, As is typically found in the +5 and +3 oxidation states [1-3]. The most common forms of As present in groundwater are the inorganic forms of arsenate ($As^{V}$) and arsenite ($As^{III}$). In areas of endemic As poisoning such as Inner Mongolia, China, groundwater is the primary drinking water source and may contain inorganic As at concentrations in the hundreds of micrograms per liter. The As in these wells is released from natural mineral deposits. Though knowledge of the total As concentration is necessary, speciation analysis is also very important as the toxicity, bioavailability, environmental persistence and treatment and removal options depend on the species of As present. Inorganic As is generally considered to be more toxic than organic As, and $As^{V}$ is typically easier to remove than $As^{III}$ from water [3,4].

The amount of particulate As in drinking water is often overlooked in studies. The amount of As adsorbed to particulate matter has been studied in natural waters [3,5-7]. However, in most studies of groundwater quality, water samples are filtered before speciation analysis takes place. Recent studies show that particulate matter can represent a significant fraction of As in groundwater [8-10] and the filtration of samples may result in an underestimation of the total As and the ineffective removal of As from groundwater. Edwards et al. examined 26 groundwater samples and 4 surface water samples from 30 utilities in 13 states and determined that particulate As concentrations ranged from 0-53% of total As in samples [8]. In the groundwater samples the particulate As averaged 18%. In groundwater affected by mine wastes, As was greater than 220 times more concentrated in suspended particulate matter than in solution [9]. Le et al. also detected particulate As in well water samples [10]. In an American study, particulate As was present at more than 50% in 30% of the samples and over 96% of As in

one groundwater sample was in particulate form. [4]. Shraim found that the total As increased significantly between unacidified tube well samples and acidified tube well samples suggesting the release of particulate As after acidification [11].

Under oxidizing conditions As may adsorb onto iron oxides, sulfide minerals and organic matter in groundwater [1,3,12,13]. Changes in environmental conditions (i.e. reducing conditions) in the wells may result in the release of As from particulate matter [1,14,15]. In particulate form, As can be removed by filtration which is much more efficient and inexpensive than other forms of treatment [4].

Two sets of water samples from Inner Mongolia are examined in this chapter. The first set of water samples were obtained from 6 wells in Inner Mongolia. They were filtered on-site and particulate and soluble As species were subsequently analyzed in the laboratory. The particulate As was captured on the filter and washed with acid to resolubilize the As. This pilot study demonstrated the presence of substantial amounts of particulate As in all well water samples. We subsequently carried out a larger scale study involving water samples from 120 wells that were each collected for 5 consecutive days. Separation and analysis took place in the laboratory. High-performance liquid chromatography hydride generation atomic fluorescence spectroscopy (HPLC-HG-AFS) was used to determine total soluble As and As species distribution. Inductively coupled plasma mass spectrometry (ICP-MS) was used to determine total As after acidification of the samples. Particulate As was calculated as the difference between total and soluble As. The results demonstrate that particulate As is present in significant concentrations in Inner Mongolia groundwater samples and is highly variable between wells.

## 4.1 Material and Methods

### 4.1.0 Instrumentation

### 4.1.1 HPLC-HG-AFS

The high performance liquid chromatography (HPLC) separation system consisted of a Gilson Model 307 pump (Middleton, WI, USA), a Rheodyne six-port sample injector (Model 7725i) with a 20 μL sample loop and a reversed-phase C18 column (ODS-3, 150 mm x 4.6 mm, 3 μm particle size; Phenomenex, Torrance, CA, USA). In addition, a C18 ODS guard cartridge (4mm L x 3.0 mm ID, Phenomenex, Torrance, CA, USA) was mounted before the analytical column to filter particles from the mobile phase and the samples and to protect the analytical column. A column heater (Model CH-30; Eppendorf) with a temperature controller (Model TC-50; Eppendorf) was used to control and maintain the HPLC column temperature. The mobile phase solution was preheated to the temperature of the column by a 50 cm precolumn coil of stainless-steel capillary tubing, which was placed inside the column heater together with the separation column. The temperature of the column was maintained at 50°C.

A hydride generation atomic fluorescence spectrometry (HGAFS) system was used as a detector for HPLC. Effluent from the HPLC column directly met at two T-joints, with continuous flows of hydrochloric acid (20% (v/v), 6 ml/min) and sodium tetrahydroborate ($NaBH_4$) (1.6% w/v, 3 ml/min) that were introduced by using a peristaltic pump. Volatile As hydrides produced in the reaction mixture were separated from liquid waste in a gas-liquid separator and were carried by a continuous flow of argon to an atomic fluorescence detector (PSA 10.055 millennium Excalibur system; PS Analytical, Kent, UK). A Pentium computer with Varian (Victoria, Australia) Star Workstation software and ADC (analog digital converter) board was used to acquire and process signals from the atomic fluorescence detector. Chromatograms were

plotted using IgorPro software (WaveMetrics, Lake Oswego, OR, USA). The HGAFS system was also used with a flow injection manifold for the analysis of total soluble As.

### 4.1.2 ICP-MS

A Perkin-Elmer 6100DRC $^{plus}$ Inductively coupled plasma-mass spectrometer (Perkin-Elmer/Sciex, USA) was used for total As elemental analysis of the water samples. The standard liquid sample introduction system consisted of a Meinhard nebulizer coupled to a cyclonic spray chamber. For sample transportation, a Gilson peristaltic pump was used. The pump was connected to the ASX-500 autosampler (CETAC technologies Inc. Omaha, Nebraska, USA) and to the Meinhard nebulizer. The flow rate for sample transportation was set to 0.8 ml/min. Instrument settings were optimized for sensitivity with a solution containing 1 $\mu$g/L each of Mg, In, Pb, Ce, Ba and Th. Mass calibration was done once every few hours. Germanium (Ge) and Scandium (Sc) were used as internal standards at concentrations of 1 $\mu$g/L each. The details of the experimental parameters are summarized in Table 4-1.

**Table 4-1. Parameter Set for ICP-MS Detection**

| basic parameter | value |
|---|---|
| RF power | 1100 W |
| Ar auxiliary gas flow rate | 1.2 L $min^{-1}$ |
| Ar plasma gas flow rate | 15 L $min^{-1}$ |
| Ar nebulizer gas flow rate | 0.90 L $min^{-1}$ |
| Dwell time | 200 ms |
| Detector mode | Dual mode |
| Scan mode | Peak hopping |
| Lens | Autolens On |
| Mass (*m/z*) | 75 |
| Rinse time | 50 seconds @ 24 rpm |
| Read delay | 15 seconds @ 18 rpm |
| Wash time | 45 seconds @ 24 rpm |
| Sweeps/Reading | 10 |
| Reading/Replicate | 1 |
| Number of Replicates | 3 |

### 4.1.3 Reagents and Solutions

All chemicals were of analytical-reagent grade unless stated otherwise. For the HPLC-HGAFS, a solution (pH 5.85) containing tetrabutylammonium hydroxide (4.7 mM, 40 wt.% in water, Aldrich Chemical Company, Milwaukee, WI), malonic acid (2mM, 99%, Fisher Scientific, Fair Lawn, NJ) and methanol (4% (v/v), Fisher Scientific) was used as the HPLC mobile phase. The flow rate was 1.2 ml/min. HCl (20% (v/v), Fisher), and sodium tetrahydroborate (1.6% (w/v), 98%, Sigma-Aldrich Canada Ltd., Oakville, ON) were used for hydride generation. For the ICP-MS analysis, $HNO_3$ (69-71% as $HNO_3$ , Fisher) was used. A Standard Reference Material (SRM1643d water) was used to confirm results. Distilled water (Millipore Milli-Q Bedford, MA, USA) was used for the preparation of standards. Stock solutions (1000 mg/L As) of $As^V$ were prepared from sodium arsenate (Sigma Chemical Co. St. Louis, MO, USA). Solutions of $As^{III}$ were prepared fresh daily from an arsenic atomic absorption standard solution (Aldrich). Standards were prepared in the concentration range of 1 μg/L to 100 μg/L.

## 4.2 Pilot Study Involving 6 Wells

### 4.2.0 Onsite Separation of $As^{III}$, $As^V$ and Particulate As

Well water samples were obtained from families in Inner Mongolia, China. The samples were filtered and As species were separated on-site to preserve the original distribution of $As^V$ and $As^{III}$. The method for on-site sampling and separation of As species with cartridges was based on that described by Le [10] (Figure 4-1). Each water sample (15ml) was allowed to pass through a filter and an anion exchange cartridge. The eluent was collected in a 15ml polyethylene tube. The filter and cartridge were disconnected and capped separately. The cartridges, filters, and eluent were sent to our laboratory for As analysis. Duplicate samples were passed through the filters and cartridge sets.

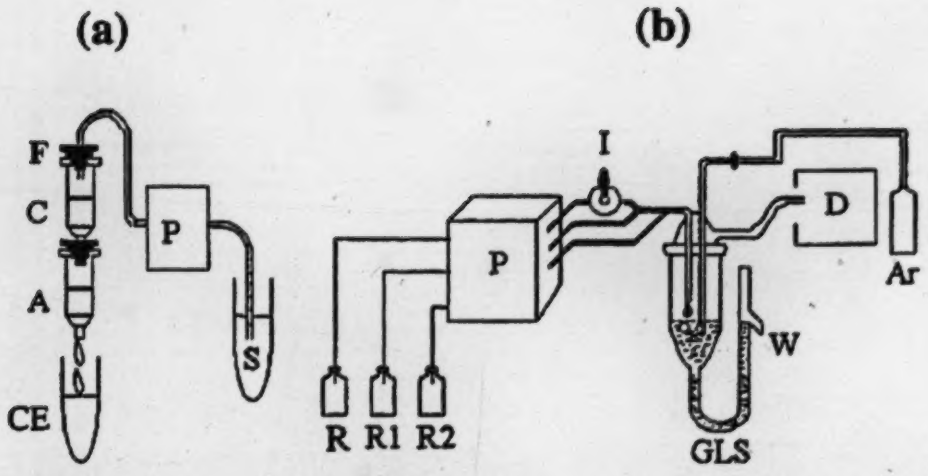


**Figure 4-1**: Schematic diagrams showing (a) a combination of cartridges and a filter in tandem for selective retention of arsenic species and (b) flow injection hydride generation for arsenic analysis. F, filter (0.45 $\mu$m); C, resin-based strong cation-exchange cartridge; A, silica-based strong anion-exchange cartridge; CE, cartridge effluent; P, peristaltic pump; S, sample; R, 0.05 M HCl; R1, 1.3% $NaBH_4$ in 0.1 M NaOH; R2, 1.2 M HCl; I, sample injector; GLS, gas-liquid separator; Ar, argon gas; D, AFS or AAS detector; W, waste. [10]

### 4.2.1 Laboratory Analysis

Particulate As collected on the membrane filters was eluted with 0.5M HCl three times at a flow rate of 1 ml /min. Each eluent fraction was analyzed separately. The sum of As determined in the three eluents divided by the volume of original water sample that was passed through the filter was reported as particulate As. Arsenate was retained on the cartridges. The cartridges were eluted twice with 1.0M HCl. Most of the $As^{V}$ was detected in the first eluent. The analysis and calculation were the same method as described for particulate As. As species eluted from the corresponding filters and cartridges and in the effluent solution were determined by using flow injection hydride generation atomic fluorescence (FI-HGAFS).

## 4.3 Second Set of Well Water Samples From 120 Wells- Analytical Procedure

### 4.3.0 Sample Collection and Storage

Before sample collection, the total As concentrations in some well waters in Inner Mongolia, China, were examined using hydride generation (cysteine reduction)-atomic fluorescence detection. According to these preliminary results, the wells were grouped into three categories: low As wells (<100 μg/L), medium As wells (100~200μg/L) and high As wells (>200μg/L). From these wells, 120 wells were chosen for the study. For each well, 5 samples were collected over 5 consecutive days. These samples were stored at –20°C. The speciation analysis and total As analysis were performed approximately four months and eight months after collection respectively.

### 4.3.1 Speciation analysis using HPLC-HGAFS detection

For HPLC-HGAFS analysis, the water samples (20 μl) were thawed and directly injected into the HPLC system without any pretreatment.

### 4.3.2 Analysis of total As concentration using ICP-MS

Prior to the particulate analysis, the water samples were thawed and then pre-acidified to 1% $HNO_3$, vortexed for 15 seconds, then allowed to stand for approximately half an hour to completely dissolve the particulate As. The pre-acidification took place in the original tubes to account for the possible adsorption of As on the walls of the plastic tubes. Before ICP-MS analysis, the pre-acidified samples were vortexed again and transferred to 15-ml tubes in which 1% $HNO_3$ was pre-added. The pH of the samples after acidification was approximately 1.4 – 1.6. Samples (1-2 mL) were transferred to 10-ml tubes, then 100µl $HNO_3$ was added and diluted to 10 ml for analysis. Similarly, all the standards were acidified to 1% $HNO_3$. HCl cannot be used to acidify the samples because of the formation of ArCl when using the ICP-MS. ArCl (*m/z* 75) would interfere with determination of As (*m/z* 75). For quality controls purposes, the results were compared to samples of SRM1643d, As spiked water samples and As standards and blanks. Additionally, an internal standard solution of Ge and Sc of 1 µg/L each was introduced on-line into the system. The equation As 75=As 75-3.127*[ArCl77-(0.815*Se 82)] was used to correct for the interference from ArCl.

## 4.4 Results

In the analysis of 120 well water samples, total As was determined by ICP-MS after the preacidification of the samples. Soluble As was detected by HPLC-HGAFS without any pretreatment of the samples. Soluble As was operationally defined as the concentration of As passing through the 0.45 µm filter mounted before HPLC analytical column and detected by HGAFS. Particulate As was calculated as the difference between total and soluble As.

To obtain the As speciation distribution in the studied water samples, the untreated samples were analyzed after thawing . These data represent the soluble As in the samples. For quality controls, three 1643d SRM samples, three As spiked water samples, six As standards (1 µg/L and 10 µg/L ), and three blank samples were separately inserted in the analysis. They were

run immediately after calibration for all sample analyses, in the middle of the analysis of the samples and after analysis of all samples. In addition, two internal standards (Ge and Sc) were introduced online to monitor the drift. The result for the 1643d SRM analysis (certified value 56.0 μg/L) was 57.7±2.6 μg/L, n=44. To ensure that As did not adsorb on the wall of the tubes during transportation and storage, the original tubes were washed with 10% $HNO_3$. The washings were analyzed on ICP-MS and the results indicated that there was no significant adsorption. The maximum concentration of As detected in the washings was 0.69 μg/L.

To examine the within-day and day-to-day repeatability of the instrument, three SRM 1643d solutions were analyzed before, half-way and after analysis of the samples during each day's 4 hours analysis, and continued for 15 days. The within-day deviations were less than 5%. The day-to-day deviations were slightly larger, but still less than 10%. Generally, there is no significant deviation and the results are acceptable. Similar experiments were carried out on some well water samples and comparable results were obtained.

In the ICP-MS analysis, the detected As should represent total As in the samples: soluble and particulate. Figure 4-2 shows the comparison of the results obtained from ICP-MS analysis with those from HPLC-HGAFS analysis. The HPLC-HGAFS results represent the total soluble As. The solid line in the figure represents perfect match between HPLC-HGAFS data and ICP-MS data, which has a slope of 1.0. The dashed line represents the linear regression between the two sets of results, which has an intercept of 44, and a slope of 1.35. The majority of the data obtained from ICP-MS analysis are above the solid line, which indicates that for many of the well water samples there is a significant amount of As present in particulate. In this analysis, particulate As is assumed to be the difference between the acidified and unacidified, filtered samples.

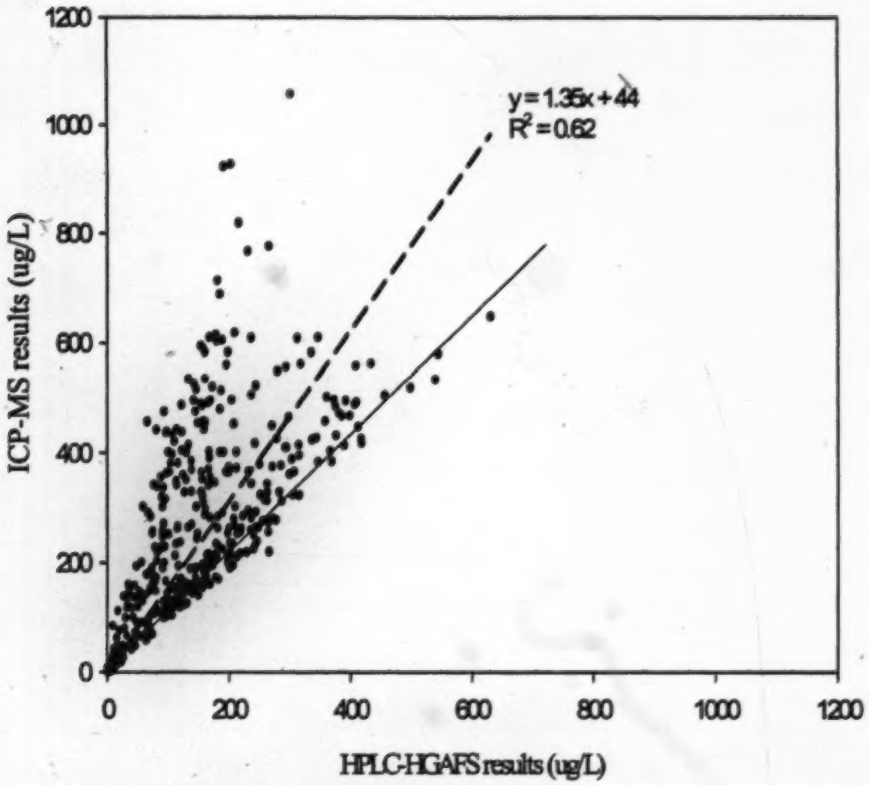


Figure 4-2: Correlation between soluble As concentration obtained by HPLC-HGAFS and total As concentration obtained by ICP-MS.

The results from the first set of water samples confirm that there is considerable particulate As present in these wells (Figure 4-3). Table 4-2 shows the results from speciation analyses of soluble $As^{III}$ and $As^{V}$ and particulate As in several well water samples collected from Inner Mongolia, China. Figure 4-3 shows the chromatogram of As species detected. The particulate As concentration in well water samples were comparable and an important contributor to the total As level in water. Particulate As represented approximately 10-22% of total As in well water respectively.

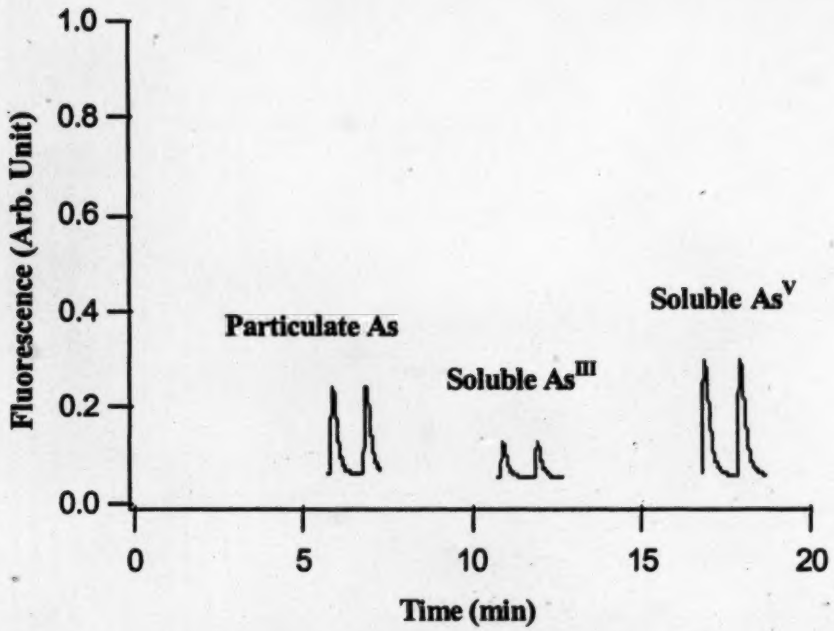


Figure 4-3: Analysis of particulate As, soluble $As^{III}$ and soluble $As^{V}$ in a well water sample from Inner Mongolia. The particulate As, soluble $As^{III}$ and $As^{V}$ species were separated on-site using a filter and anion exchange cartridge set-up (Figure 4-1).

Table 4-2: Arsenic Speciation Analysis in Inner Mongolia Well Water Samples*

| Sample | $As^{III}$ (μg/L) | $As^{V}$ [a] (μg/L) | Particulate As[b] (μg/L) | Sum (μg/L) |
|---|---|---|---|---|
| 1 | 419.9 | 132.0 | 119.3 | 671.2 |
| 2 | 153.3 | 128.6 | 81.0 | 362.9 |
| 3 | 493.6 | 152.0 | 88.5 | 734.1 |
| 4 | 193.7 | 175.4 | 91.1 | 460.2 |
| 5 | 281.3 | 132.3 | 46.1 | 459.7 |
| 6 | 183.3 | 126.7 | 60.5 | 370.6 |

[a] $As^{V}$ retained on cartridges
[b] As retained on filters
*Concentrations are presented as mean values

## 4.5 Discussion

Speciation studies are necessary to determine the individual As species present in natural waters. The species of As present will determine its environmental mobility, bioavailability, and optimum treatment and removal methods. In many studies, the soluble As species are assumed to be predominant in natural waters, however particulate As may also be present in significant amounts. In the present study, particulate As represented approximately 30% in the pilot study of well water and in the larger scale study of 120 well water samples. There was an approximate 30 percent increase in total As after acidification of the unfiltered samples which presumably represents particulate As. Particulate As is likely filtered out and not detected in the speciation analysis using HPLC-HGAFS resulting in the detection of lower As concentrations.

The failure to determine the amount of As associated with particulate matter may result in an underestimation of the total As present in the wells. Changes in geochemical conditions in the well water may result in a significant release of As from the particulate. It was assumed that the difference is due to the composition of the samples, mainly the Fe content. The difference

between the two samples appeared to be highest when a brownish precipitate was observed at the bottom of the tubes of the unacidified samples [11]. For two samples, the sum of As species was 526.4μg/L and 602.9μg/L for the acidified samples and 62.4μg/L and 143.1μg/L in the unacidified samples. However, there is no discussion of the implications of the presence of particulate As in that study [11].

Effective treatment and removal methods need to be developed to remove As from drinking water. The optimum treatment and removal of As from drinking water depends on the species of As present. For example, $As^{V}$ is easier to remove than $As^{III}$ by using anion exchange methods. Pretreatment such as the oxidation of $As^{III}$ is often necessary and can be very costly [4]. However, particulate As can easily and inexpensively be removed by filtration [3,4]. If a substantial amount of As is associated with particulate, then acceptable As levels may be attained by filtration alone. The toxicity of As also depends on the species present and inorganic As is generally considered to be more toxic than organic As. The ingestion of particulate As will presumably result in the desorption of inorganic As under the acidic conditions in the human gastrointestinal system.

In this study, total As concentrations varied significantly between wells and within wells. Between wells the total As concentration ranged from <1-900 μg/L (Figure 4-4a and 4-4b) . This type of short-range variation has been noted in other studies [11,16]. In a study of groundwater in Argentina the As concentrations varied from <4-3500 μg/L [16]. One explanation in this study was that this difference was likely due to the restriction of groundwater movement in some areas and the resultant poor mixing of the groundwater. In West Bengal, there was a wide variation in the total As concentration detected between wells collected from the same area [11].

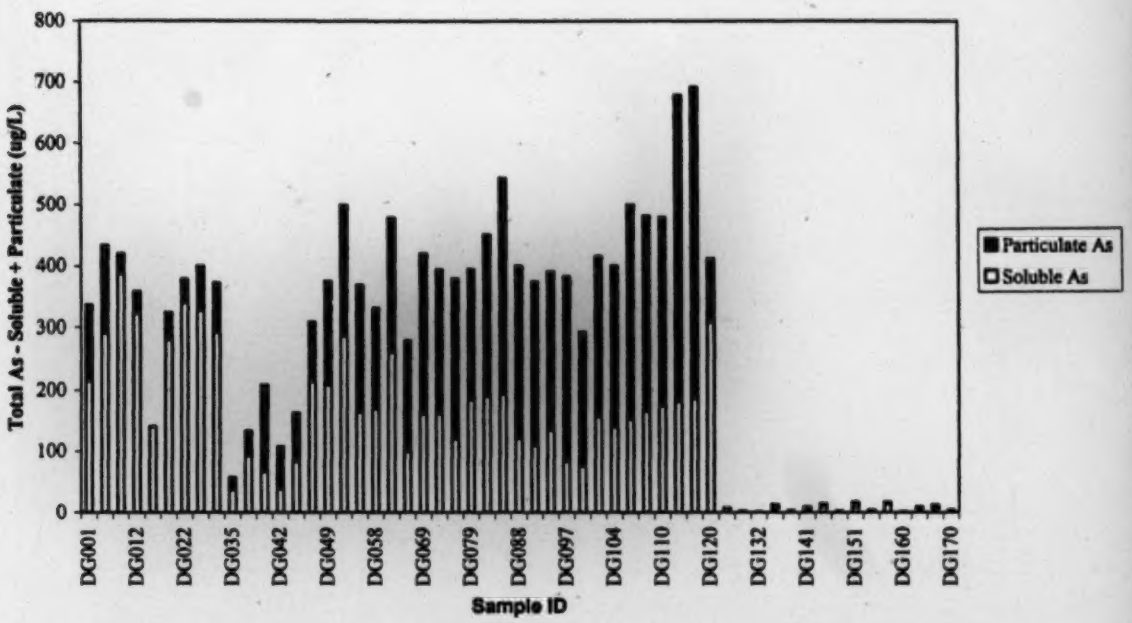


Figure 4-4a: Variation of particulate and soluble As distribution between wells in Inner Mongolia

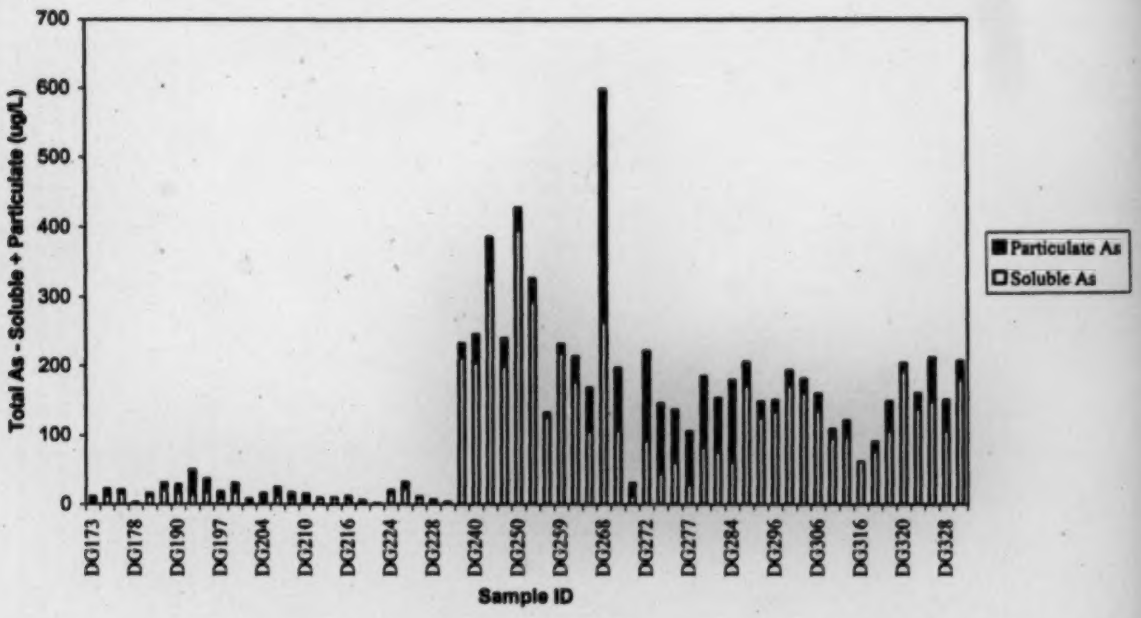


Figure 4-4b: Variation of particulate and soluble As distribution between wells in Inner Mongolia

There is also daily variation in the total As concentrations within each well. This may be due to a daily variation in the amount of particulate As in the wells. A change in the amount of As adsorbed and coprecipitated with particulate matter may be caused by changing chemical conditions in the water such as pH, ionic strength, the amount of particulate matter, and the concentration of competing ions [1,3,17]. Due to the short-term nature of most studies, the cause for the variation can not be explained. The difference could also be due to the incomplete dissolution of all of the particulate As in the samples. There may also be a problem with the homogeneity of the samples resulting in a misrepresentation of the amount of particulate As in the wells. In a recent study, it was determined that there was no significant particulate As in 211 samples collected in Mandari village, south-eastern Bangladesh in November 1999 [18]. This conclusion was based on comparing the speciation analysis results of two different methods. However, without longer term studies, these results are not necessarily representative of the common conditions in the wells.

When comparing findings in the literature, one must take into consideration the authors definition of particulate As. The operational definition of particulate arsenic is particularly important. For example, in one study, a 0.02 μm filter removed 50-60 percent of total As and iron colloids from samples [8]. However, when the same samples were passed through a 0.45μm filter, only 3-40 percent of the total As was removed [8]. Therefore, an investigator's finding may not represent the total amount of As adsorbed to particulate and the total As concentration could be underestimated. A complete definition of particulate As should include the size of the filter.

### 4.6 Concluding Remarks

The presence of particulate As in drinking water supplies deserves more attention. It is clear that particulate As contributes significantly to the total As in well water in Inner Mongolia and other countries. The determination of particulate As in the well water is important with regards to the effective treatment and removal of As from drinking water. Filtration may remove enough As to bring the level to below guidelines.

Speciation studies are important because the toxicity of As will vary depending on the species. The health effects of exposure to inorganic and organic As species have been and continue to be studied extensively. However, the clinical significance of particulate As is also not known. Further research is needed to determine if the health effects of ingesting particulate As differ from those that occur from ingesting soluble As species.

The concentration of As in groundwater varies between wells and within wells. Longer term studies are also needed to provide information on the variation of particulate As in the wells. It is important to determine how much of this variation is due to analytical techniques and how much is due to natural processes. Smaller studies should be nested within the long term study to analyze variations over shorter time periods such as weeks and months.

## 4.7 References


[1] A.H. Welch, Ground water 38 (2000) 589.

[2] A.H. Welch, M.S. Lico, J.L. Hughes, Ground Water 26 (1988) 333.

[3] W.R. Cullen, K.J. Reimer, Chem. Rev. 89 (1989) 713.

[4] H.W. Chen, M.M. Frey, D. Clifford, L.S. McNeill, M. Edwards, J. Am. Water Works. Assoc. 91 (1999) 74.

[5] P. Michel, B. Boutier, A. Herbland, B. Averty, L.F. Artigas, D. Auger, E. Chartier, Oceanol. Acta 21 (1997) 325.

[6] A.R. Abdel-Moati, Wat. Air. Soil. Pollut. 51 (1990) 117.

[7] A.G. Howard, M.H. Arbab-Zavar, S.C. Apte, Estuar. Coast Shelf Sci. 19 (1984) 493.

[8] M. Edwards, S. Patel, L. McNeill, H.W. Chen, M.M. Frey, A.D. Eaton, R.C. Antweiler, H.E. Taylor, J. Am. Water Works. Assoc. 90 (1998) 103.

[9] C. Roussel, H. Bril, A. Fernandez, J. Environ. Qual. 29 (2000) 182.

[10] X.C. Le, S. Yalcin, M. Ma, Environ. Sci. Technol. 34 (2000) 2342.

[11] A. Shraim, N.C. Sekaran, C.D. Anuradha, S. Hirano, Appl. Organometal. Chem. 16 (2002) 202.

[12] J.F. Ferguson, J. Gavis, Wat. Res. 6 (1972) 1259.

[13] NRC, Arsenic in Drinking Water, National Academy Press, Washington, DC, 1999.

[14] R. Nickson, J. MCarthur, W. Burgess, K.M. Ahmed, P. Ravenscroft, M. Rahmann, Nature 395 (1998) 338.

[15] R.T. Nickson, J.M. McArthur, P. Ravenscroft, W.G. Burgess, K.M. Ahmed, Appl. Geochem. 15 (2000) 403.

[16] P.L. Smedley, H.B. Nicolli, D.M.J. Macdonald, A.J. Barros, J.O. Tullio, Appl. Geochem. 17 (2002) 259.

[17] P.L. Smedley, D.G. Kinniburgh, Appl. Geochem. 17 (2002) 517.

[18] D.G. Kinniburgh, W. Kosmus, Talanta 58 (2002) 165.

## 5.0 Concluding Remarks and Future Research

Arsenic occurs naturally in the environment and high levels of As in aquatic systems can pose a serious hazard to health of humans and the environment. Both inorganic and methylated As species have been detected in aquatic systems. Inorganic $As^{V}$ and $As^{III}$ are predominant in most natural waters while methylated arsenic species occur at much lower concentrations. Arsenothiols, particulate and uncharacterized As species are also present in some water environments. The ingestion of inorganic As from drinking water is the most common route of exposure and is a risk factor for several cancers and non-cancerous health effects.

Arsenic is involved in many biological processes in the aquatic environment. The determination of total arsenic is not sufficient to study its biogeochemical cycle and to predict the potential toxicity to humans and aquatic ecosystems. A knowledge of the speciation and transformations of As in natural water is important because the bioavailability and the physiological/toxicological effects of As depend on its chemical form. The species of As present control not only its toxicity but its transport mechanisms and environmental persistence. Arsenic speciation and distribution is affected by redox processes complicated by physicochemical processes such as adsorption, coprecipitation, and desorption and biological phenomena such as uptake and regeneration.

The instability of arsenic species in water samples and the procedures used for sample handling and analysis may be the reason that $As^{V}$ is commonly reported as the predominant species in water. Species preservation and sampling handling method development is important. However, the stability of As compounds depends on the species present and there have been limited consistent results reported regarding the preservation of $As^{III}$ and $As^{V}$ for extended periods of time. The development of robust, sensitive and accurate analytical techniques that are

suitable for field measurements of As in water must be further investigated. The determination of arsenic species and their distribution is of crucial importance for reducing the cost of drinking water treatment and to protect human health. Both improved analytical techniques and the knowledge of source contribution of As will help to make more accurate assessments on the environmental impact and health risks posed by this compound.

The concentration of As and the distribution of As species (including particulate As) varies considerably between wells and within wells. Therefore, it may be difficult to predict the concentration of As in a particular well from the results of neighbouring wells. There is little alternative but to analyze each well. Taking this into account, it is necessary to develop rapid and efficient methods for determining As species in water. The solid phase extraction cartridges provide separation of $As^{III}$ and $As^{V}$ in under 5 minutes, can handle a high volume of samples and are relatively inexpensive.

The failure to determine particulate As in well water results in an underestimation of the total As present. Particulate As represents a significant portion of total As in well water. By ignoring this fraction, we are likely underestimating the total As in groundwater. The health effects of particulate have not been investigated and this issue deserves attention. Longer term studies on groundwater are needed to fully understand the temporal and seasonal variation of As in well water and particulate As. Nested short term studies within these long term studies will provide information on daily and weekly variation. It is difficult to ascertain whether daily variation in As levels is due to variations in sampling and analysis procedures or truly represent the original As level in the well. One possibility for the variation is that the particulate fraction of As varies markedly between days. The determination of particulate As during one month of investigation is not necessarily representative of the average values as the system may not be in a state of equilibrium. It is important to determine the particulate fraction of As because optimum

treatment options depend on As species present in water. Particulate As can be removed relatively inexpensively by filtration.

Finally, substantial amounts of arsenic species remain to be characterized. One of the most important aspects of future research will be to identify these uncharacterized As species. In seawater these species can be present in significant levels. The identification of these species will help complete the picture on the biogeochemistry of As in the environment with an emphasis on the biological transformation of As and As mobility in aqueous systems.